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Asymmetric Catalytic [4+3] Cycloaddition of *ortho*-Quinone Methides with Oxiranes

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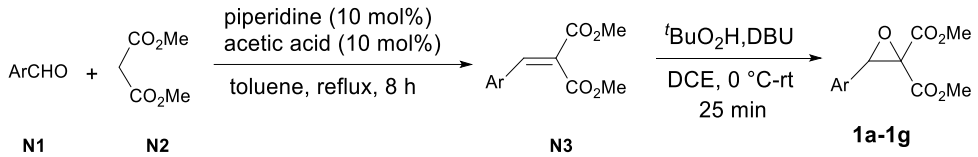
1 General Remarks

^{1}H NMR (400M) spectra were recorded on bruker ASCEND^{TM} 400M. Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), coupling constants (Hz), integration. ^{13}C{^{1}H} NMR data were collected on bruker ASCEND^{TM} 400M (101M) with complete proton decoupling. Chemical shifts were reported in ppm relative to tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.16). ^{19}F{^{1}H} NMR spectra were collected on bruker ASCEND^{TM} 400M (376 MHz) with complete proton decoupling. Enantiomeric excesses were determined by chiral HPLC analysis on Daicel Chiralcel IA, IB, ID at 23 °C with UV detector at 254 nm in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]^T_D$ (λ = 589 nm, *c*: g/100 mL, in CH_2Cl_2). HRMS was recorded on Thermo Q-Exactive Focus (FTMS+c ESI). IR was detected by Bruker Tensor II spectrometer with Plantium ATR accessory. All the solvents were purified by usual methods before use. Silica gel for thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd. Chiral *N*,*N*′-dioxide ligands were prepared according to previously reported method.[1]

2 General Reaction for the Synthesis of Oxiranes

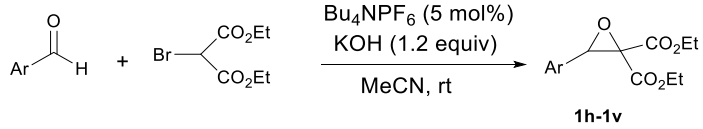
Route 1.



N1 **N2** **N3** **1a-1g**

The mixture of aldehyde **N1** (50 mmol), dimethyl manolate **N2** (60 mmol), piperidine (426 mg, 5 mmol) and acetic acid (300 mg, 5 mmol) were dissolved in toluene at room temepreture, then the system was heated to reflux for 6 hours (separate the produced water from the system). After the reaction was completed (monitored by TLC), the solvent was removed under reduced pressure, and the obtained mixture was dissolved in dichloromethane and diluted with H_2O (25 mL). The organic layer was washed withed Na_2SO_3 (20 mL) and brine (20 mL), then dried with Na_2SO_4, filtered. The solvent was removed and the residue was purified by silica gel column chromatography eluting with petroleum ether/ethyl acetate = 25:1, and the compound **N3** was obtained as a colorless oil (58%-93% yield). The method for synthesis of oxiranes **(1a-1g)** were prepared according to the procedure.[2]

Route 2.

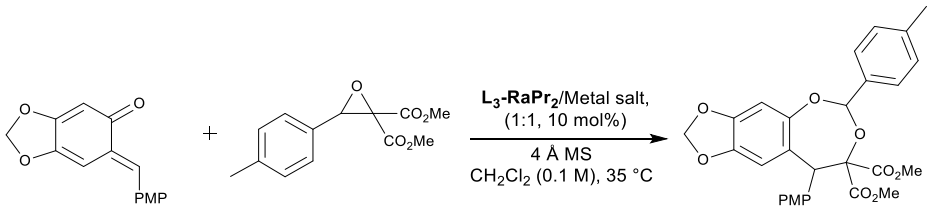


1h-1v

The substrate **(1h-1v)** were prepared according to the literature procedure.[3]

3 Optimization of Reaction Conditions

Table S1. Screening of metal salts in the asymmetric catalytic [4+3] cycloaddition reaction of **1a**.



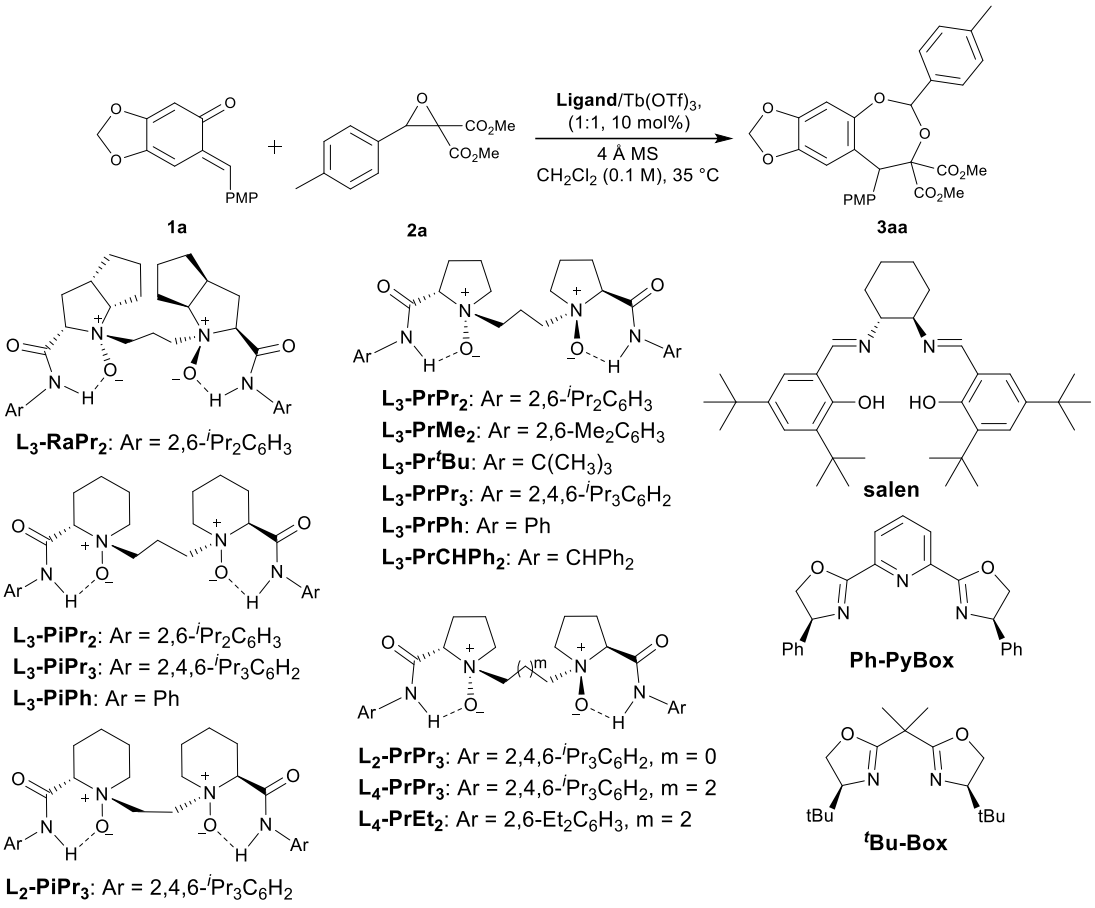
1a **2a** **3aa**

entry[a]	metal salt	yield (%)[b]	ee (%)[c]	dr[c]
1	$Ni(OTf)_2$	NR	-	-
2	$Sc(OTf)_3$	NR	-	-
3	$Y(OTf)_3$	18	7	72:28
4	$La(OTf)_3$	trace	-	-

5	$Ce(OTf)_3$	trace	-	-
6	$Pr(OTf)_3$	trace	-	-
7	$Nd(OTf)_3$	30	0	80:20
8	$Sm(OTf)_3$	25	11	82:12
9	$Eu(OTf)_3$	55	0	81:29
10	$Gd(OTf)_3$	33	6	82:18
11	**$Tb(OTf)_3$**	**38**	**15**	**83:17**
12	$Dy(OTf)_3$	25	5	72:28
13	$Ho(OTf)_3$	36	0	71:29
14	$Er(OTf)_3$	32	8	75:25
15	$Tm(OTf)_3$	27	6	75:25
16	$Yb(OTf)_3$	30	3	73:27
17	$Lu(OTf)_3$	trace	-	-

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.12 mmol), **2a** (0.10 mmol), metal salt/**L_3-RaPr$_2$** (1:1, 10 mol%), 4 Å MS (60 mg) in dichloromethane (1.0 mL) at 35 °C for 24 h. [b] Yield of the isolated products. [c]Determined by HPLC analysis on a chiral stationary phase.

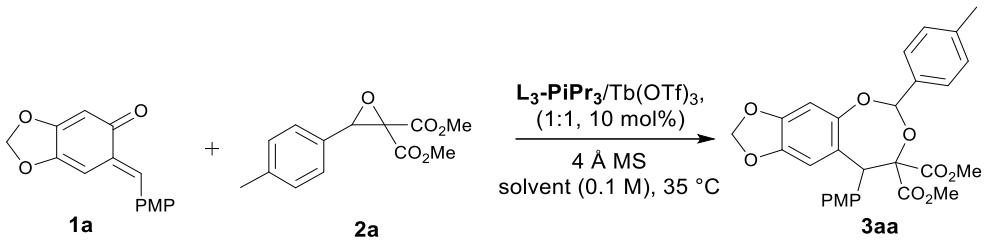
Table S2. Screening of the ligands in the asymmetric catalytic [4+3] cycloaddition reaction of **1a**.



entry[a]	ligand	yield (%)[b]	ee (%)[c]	dr[c]
1	**L_3-$PrPr_2$**	96	37	90:10
2	**L_3-$RaPr_2$**	38	15	80:20
3	**L_3-$PiPr_2$**	65	36	87:13
4	**L_3-PrPh**	53	30	85:15
5	**L_3-$PrMe_2$**	66	6	86:14
6	**L_3-Pr^{t}Bu**	64	19	84:16
7	**L_3-$PrCHPh_2$**	89	16	86:14
8	**L_3-$PrPr_3$**	99	28	85:15
9	**L_2-$PrPr_3$**	99	5	76:24
10	**L_4-$PrPr_3$**	80	29	85:15
10	**L_4-$PrEt_2$**	89	20	88:12
11	**L_3-PiPh**	NR	-	-
12	**L_2-$PiPr_3$**	76	6	80:20
13	**L_3-$PiPr_3$**	**62**	**66**	**88:12**
14	**Salen**	51	0	78:22
15	**Ph-PyBox**	32	47/20	68:32
16	**^{t}Bu-Box**	trace	-	-

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.12 mmol), **2a** (0.10 mmol), **ligand**/$Tb(OTf)_3$ (1:1, 10 mol%), 4 Å MS (60 mg) in dichloromethane (1.0 mL) at 35 °C for 24 h. [b] Yield of the isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S3. Screening of the solvents in the asymmetric catalytic [4+3] cycloaddition reaction of **1a**.

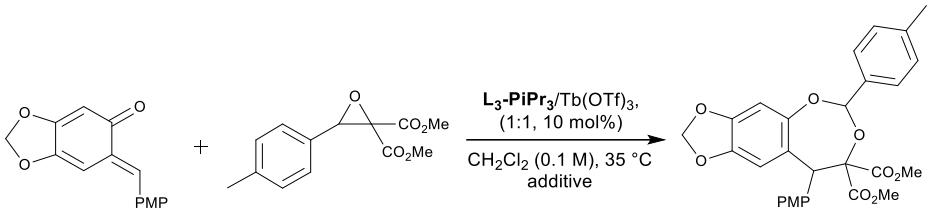


1a **2a** **3aa**

entry[a]	solvent	yield (%)[b]	ee (%)[c]	dr[c]
1	CH_2ClCH_2Cl	68	63	93:7
2	**CH_2Cl_2**	**62**	**66**	**88:12**
3	$CHCl_2CH_2Cl$	26	61	93:7
4	$CHCl_2CHCl_2$	61	60	90:10
5	$CHCl_3$	56	60	85:15
6	Toluene	NR	-	-
7	Et_2O	NR	-	-
8	EtOAc	NR	-	-
9	THF	NR	-	-

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.12 mmol), **2a** (0.10 mmol), **L_3-$PiPr_3$**/$Tb(OTf)_3$ (1:1, 10 mol%), 4 Å MS (60 mg) in solvent (1.0 mL) at 35 °C for 24 h. [b] Yield of the isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S4. The screening of additives in the asymmetric catalytic [4+3] cycloaddition reaction of **1a**.

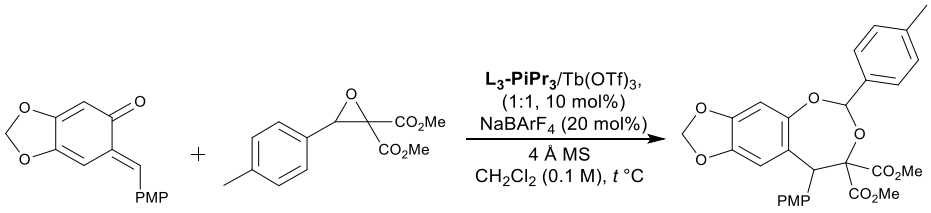


1a **2a** **3aa**

entry[a]	additives	yield (%)[b]	ee (%)[c]	dr[c]
1	-	NR	-	-
2	3 Å MS (60 mg)	71	59	90:10
3	4 Å MS (60 mg)	62	66	88:12
4	5 Å MS (60 mg)	51	56	92:8
5	4 Å MS (60 mg) + $LiNTf_2$ (10 mol%)	95	72	88:12
6	4 Å MS (60 mg) + $NaBArF_4$ (10 mol%)	99	87	88:12
7	**4 Å MS (60 mg) + $NaBArF_4$ (20 mol%)**	**99**	**92**	**80:20**
8	4 Å MS (60 mg) + $NaBArF_4$ (30 mol%)	99	92	63:37

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.12 mmol), **2a** (0.10 mmol), /**L_3-PiPr$_3$/**Tb(OTf))$_3$ (1:1, 10 mol%), additive, in dichloromethane (1.0 mL) at *t* °C for 24 h. [b] Yield of the isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S5. The screening of temperature in the asymmetric catalytic [4+3] cycloaddition reaction of **1a**.

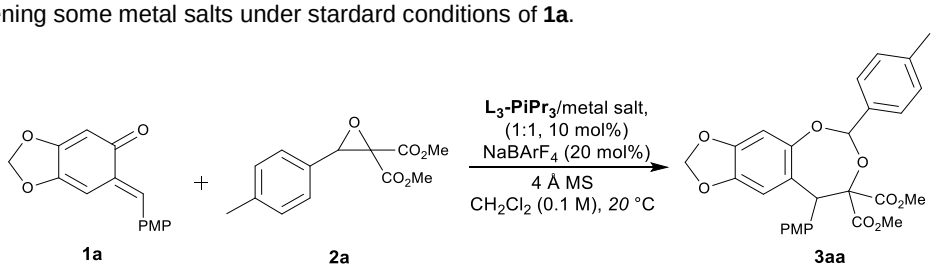


1a **2a** **3aa**

entry[a]	*t* °C	yield (%)[b]	ee (%)[c]	dr[c]
1	**20**	**99**	**96**	**89:11**
2	35	99	92	80:20

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.12 mmol), **2a** (0.10 mmol), **L_3-PiPr$_3$**/Tb(OTf))$_3$ (1:1, 10 mol%), 4 Å MS (60 mg) and $NaBArF_4$ (20 mol%) in dichloromethane (1.0 mL) at *t* °C for 24 h. [b] Yield of the isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S6. Rescreening some metal salts under stardard conditions of **1a**.



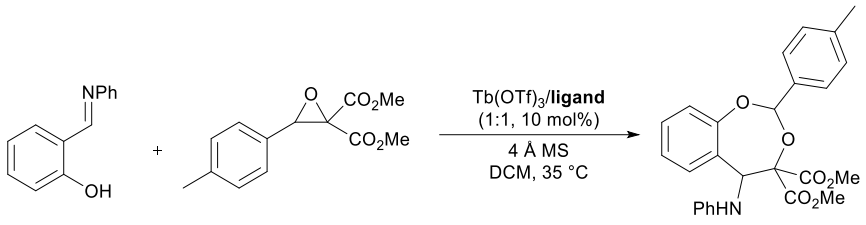
1a **2a** **3aa**

entry[a]	metal salt	yield (%)[b]	ee (%)[c]	dr[c]

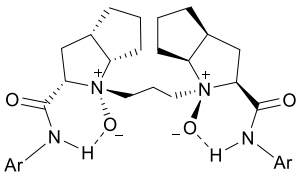
1	$Y(OTf)_3$	88	86	88:12
2	$Gd(OTf)_3$	82	82	88:12
3	$Ho(OTf)_3$	87	80	86:14

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.12 mmol), **2a** (0.10 mmol), **L_3-PiPr$_3$**/metal salt (1:1, 10 mol%), 4 Å MS (60 mg) and $NaBArF_4$ (20 mol%) in dichloromethane (1.0 mL) at 20 °C for 24 h. [b] Yield of the isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.

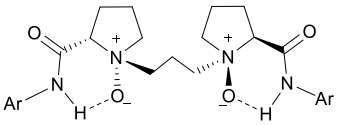
Table S7. Screening of the ligands in the asymmetric catalytic [4+3] cycloaddition reaction of **1d**.



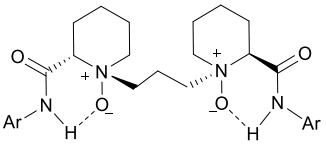
1d **2a** **3da**



L_3-RaPr$_2$: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$



L_3-PrPr$_2$: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$
L_3-Pr^{t}Bu: Ar = $C(CH_3)_3$
L_3-PrPr$_3$: Ar = 2,4,6-^{i}Pr$_3$C$_6$H$_2$
L_3-PrPh: Ar = Ph
L_3-PrCHPh$_2$: Ar = $CHPh_2$
L_3-PrCPh$_3$: Ar = CPh_3
L_3-PrCp: Ar = C_5H_9

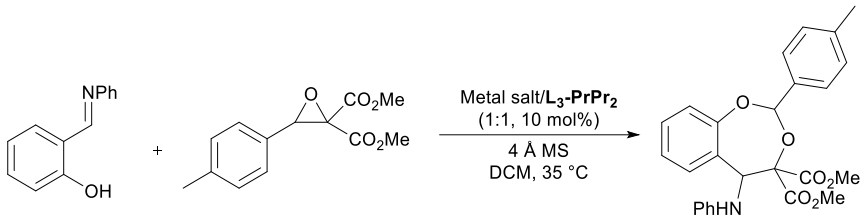


L_3-PiPr$_2$: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$
L_3-PiPr$_3$: Ar = 2,4,6-^{i}Pr$_3$C$_6$H$_2$
L_3-PiPh: Ar = Ph
L_3-PiEt$_2$: Ar = 2,6-Et$_2$C$_6$H$_3$

entry[a]	ligand	yield (%)[b]	ee (%)[c]	dr[c]
1	**L_3-PrPr$_2$**	51	30	>19:1
2	**L_3-RaPr$_2$**	43	30	>19:1
3	**L_3-PiPr$_2$**	47	19	>19:1
4	**L_3-PrPh**	56	14	91:9
5	**L_3-Pr^{t}Bu**	60	3	88:12
6	**L_3-PrCHPh$_2$**	27	5	>19:1
7	**L_3-PrCPh$_3$**	trace	-	-
8	**L_3-PrCp**	trace	-	-
9	**L_4-PrAd**	56	20	>19:1
10	**L_3-PiPh**	31	37	>19:1
11	**L_3-PiEt$_2$**	58	20	>19:1
12	**L_3-PiPr$_3$**	54	20	>19:1
13[d]	**L_3-PiPr$_3$**	20	21	>19:1

[a] Unless otherwise noted, all reactions were carried out with **1d** (0.12 mmol), **2a** (0.10 mmol), **ligand**/$Tb(OTf))_3$ (1:1, 10 mol%), 4 Å MS (60 mg) in dichloromethane (1.0 mL) at 35 °C for 24 h. [b] Yield of the isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.[d] with 10 mol% $NaBArF_4$.

Table S8. Screening of metal salts in the asymmetric catalytic [4+3] cycloaddition reaction of **1d**.

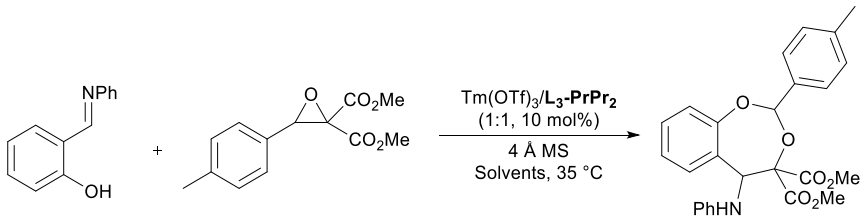


1d **2a** **3da**

entry[a]	metal salt	yield (%)[b]	ee (%)[c]	dr[c]
1	$Mg(OTf)_2$	NR	-	-
2	$Ni(OTf)_2$	NR	-	-
3	$Sc(OTf)_3$	NR	-	-
4	$Y(OTf)_3$	54	45	>19:1
5	$Ce(OTf)_3$	13	5	>19:1
6	$Nd(OTf)_3$	29	17	>19:1
7	$Eu(OTf)_3$	23	25	>19:1
8	$Tb(OTf)_3$	51	30	>19:1
9	$Ho(OTf)_3$	36	38	>19:1
10	$Tm(OTf)_3$	45	51	>19:1

[a] Unless otherwise noted, all reactions were carried out with **1d** (0.12 mmol), **2a** (0.10 mmol), metal salt/**L3-PrPr2** (1:1, 10 mol%), 4 Å MS (60 mg) in dichloromethane (1.0 mL) at 35 °C for 24 h. [b] Yield of the isolated products. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S9. Screening of the solvents in the asymmetric catalytic [4+3] cycloaddition reaction of **1d**.

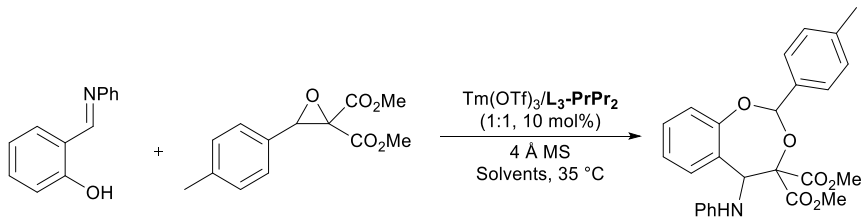


1d **2a** **3da**

entry[a]	solvent	yield (%)[b]	ee (%)[c]	dr[c]
1	CH_2Cl_2	45	51	>19:1
2	$CHCl_2CH_2Cl$	trace	-	-
3	$CHCl_3$	20	48	>19:1
4	Toluene	NR	-	-
5	Et_2O	NR	-	-
6	MTBE	NR	-	-
7	THF	NR	-	-
8	MeOH	NR		

[a] Unless otherwise noted, all reactions were carried out with **1d** (0.12 mmol), **2a** (0.10 mmol), **L3-PrPr2**/$Tm(OTf))_3$ (1:1, 10 mol%), 4 Å MS (60 mg) in solvent (1.0 mL) at 35 °C for 24 h. [b] Yield of the isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S10. Screening of the additives in the asymmetric catalytic [4+3] cycloaddition reaction of **1d**.

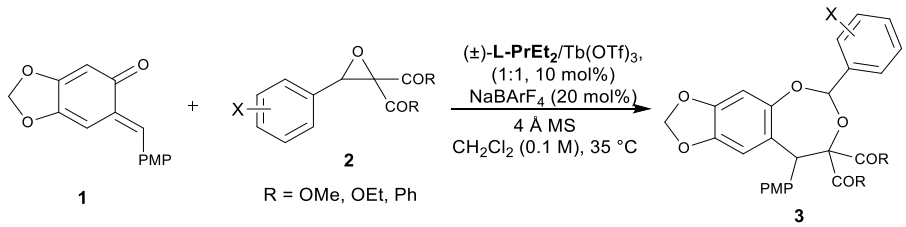


1d **2a** **3da**

entry[a]	additives	yield (%)[b]	ee (%)[c]	dr[c]
1	-	NR	-	-
2	3 Å MS (60 mg)	trace	-	-
3	4 Å MS (60 mg)	45	51	>19:1
4	5 Å MS (60 mg)	38	46	>19:1
5	4 Å MS (20 mg)	16	51	>19:1
6	4 Å MS (40 mg)	36	51	>19:1

[a] Unless otherwise noted, all reactions were carried out with **1d** (0.12 mmol), **2a** (0.10 mmol), **L_3-PrPr$_2$**/Tm(OTf))$_3$ (1:1, 10 mol%), additive, in dichloromethane (1.0 mL) at 35 °C for 24 h. [b] Yield of the isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.

4 General Procedure for the Preparation of the Racemic Products



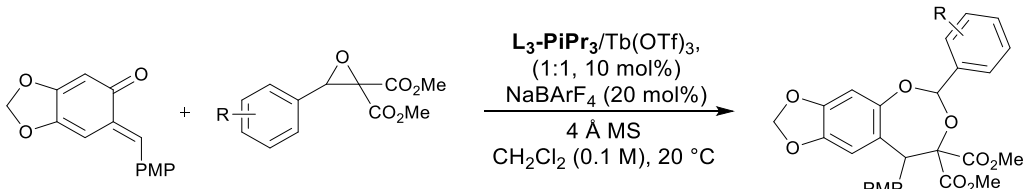
1 **2** **3**

R = OMe, OEt, Ph

An oven-dried test tube was charged with **1** (0.12 mmol), **2** (0.10 mmol), Tb(OTf)$_3$ (10 mol%), (±)-**L_3-PrEt$_2$** (10 mol%), NaBArF$_4$ (20 mol%), 4 Å MS (60 mg) and CH_2Cl_2 (1.0 mL). The reaction mixture was stirred at 35 °C for 24 h and detected by TLC. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1) to afford the racemic product **3**.

5 General Procedure for the Asymmetric Catalytic [4+3] Cycloaddition Reaction

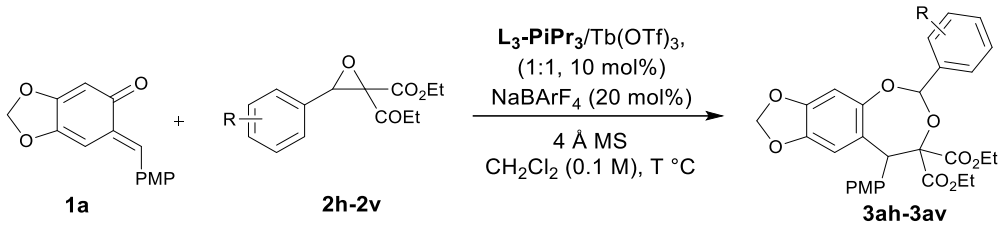
Route 1



1a-1d **2a-2g** **3aa-3ag, 3ba-3da**

An oven-dried test tube was charged with **L_3-PiPr$_3$** (0.01 mmol, 10 mol%), Tb(OTf)$_3$ (0.01 mmol, 10 mol%), NaBArF$_4$ (20 mol%), 4 Å MS (60 mg) and CH_2Cl_2 (1.0 mL) under N_2 atmosphere and the resulting solution was stirred at 30 °C for 30 min. After this procedure**,** **1a-1c** (0.12 mmol), **2a-2g** (0.10 mmol) were added into the tube. Then, the reaction mixture was stirred at 20 °C and detected by TLC. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1) to afford the products **3aa-3ag, 3ba-3da**.

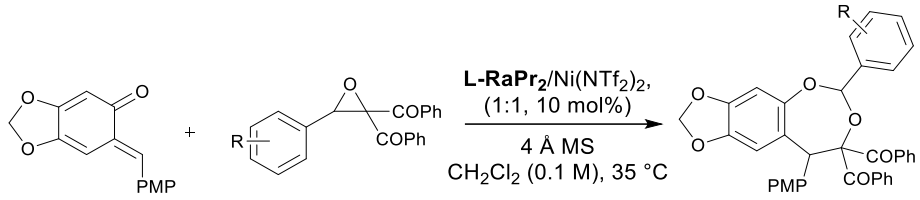
Route 2



1a **2h-2v** **3ah-3av**

An oven-dried test tube was charged with **L_3-PiPr$_3$** (0.01 mmol, 10 mol%), $Tb(OTf)_3$ (0.01 mmol, 10 mol%), $NaBArF_4$ (20 mol%) and CH_2Cl_2 (1.0 mL) and the resulting solution was stirred at 30 °C for 30 min. After this procedure, 4 Å MS (60 mg), **1a** (0.12 mmol) and **2h-2v** (0.10 mmol) were weighted into the tube. Then, the reaction mixture was stirred at corresponding temperture and detected by TLC. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1) to afford the enantioenriched product **3ah-3av**.

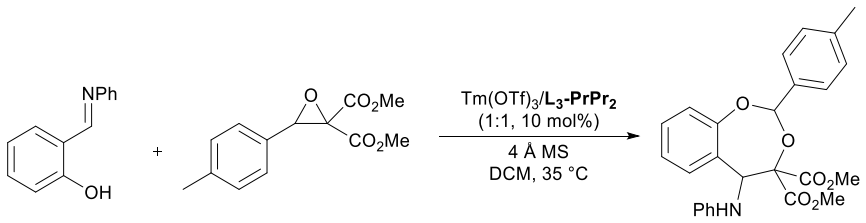
Route 3



1a **2w-2x** **3aw-3ax**

An oven-dried test tube was charged with **L_3-RaPr$_2$** (0.01 mmol, 10 mol%), $Ni(NTf_2)_2$ (0.01 mmol, 10 mol%), 4 Å MS (60 mg) and CH_2Cl_2 (1.0 mL) under N_2 atmosphere and the resulting solution was stirred at 30 °C for 30 min. After this procedure**,** **1a** (0.12 mmol), **2w-2x** (0.10 mmol) were weighted into the tube. Then, the reaction mixture was stirred at 35 °C and detected by TLC. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1) to afford the enantioenriched product **3av-3ax**.

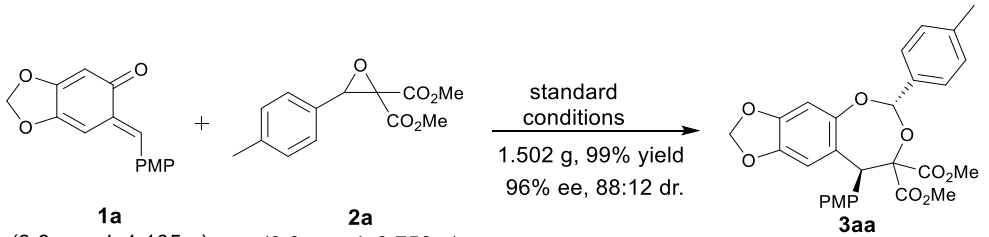
Route 4



1d **2a** **3da**

An oven-dried test tube was charged with **L_3-PrPr$_2$** (0.01 mmol, 10 mol%), $Tm(OTf)_3$ (0.01 mmol, 10 mol%), 4 Å MS (60 mg) and CH_2Cl_2 (1.0 mL) under N_2 atmosphere and the resulting solution was stirred at 35 °C for 30 min. After this procedure**,** **1d** (0.12 mmol), **2a** (0.10 mmol) were weighted into the tube. Then, the reaction mixture was stirred at 35 °C and detected by TLC. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 9:1) to afford the enantioenriched product **3da**.

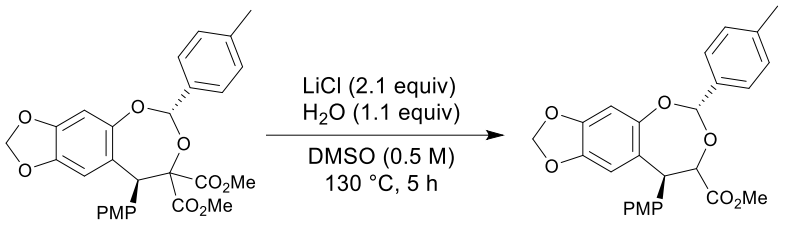
6 Experimental Procedure for the Gram-Scale Reaction and Transformations of the Products



1a (3.6 mmol, 1.105 g) **2a** (3.0 mmol, 0.750 g) **3aa**

After recrystallization: 93% yield, 99% ee, >19:1 dr.

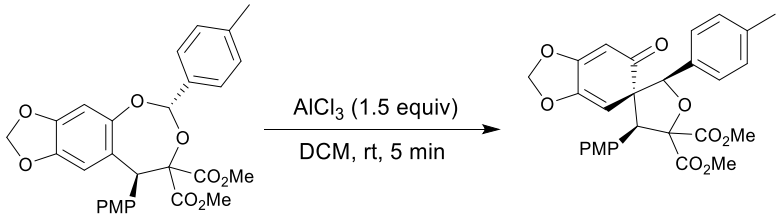
An over dried test tube was charged with **L_3-PiPr$_3$** (0.3 mmol, 10 mol%), $Tb(OTf)_3$ (0.3 mmol, 10 mol%), $NaBArF_4$ (531 mg, 20 mol%), 4 Å MS (1.8 g) and CH_2Cl_2 (30.0 mL) under N_2 atmosphere and the resulting solution was stirred at 35 °C for 30 min. After this procedure, **1a** (3.6 mmol), **2a** (3.0 mmol) were added into the tube. Then, the reaction mixture was stirred at 20 °C and detected by TLC. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1) to afford the enantioenriched product **3aa** (1.50 g, 99% yield, 96% ee, 88:12 dr), then recrystallized by dichloromethane/ petroleum ether to afford the purified product (93% yield, 99% ee, >19:1 dr).



3aa **4a**

78% yield, 99/96% ee, 65:35 d.r.

An oven-dried test tube was charged with **3aa** (0.3 mmol, 151.8 mg, 99% ee, >19:1 dr) and DMSO (0.5 M) followed by adding LiCl (2.1 equiv) and H_2O (1.1 equiv). The reaction mixture was stirred at 130 °C for 5 hours and detected by TLC. After the reaction was completed, the reaction was quenched with EtOAc/H_2O (3 mL/3 mL)and extracted with EtOAc (2×10 mL). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1) to afford the desired product **4a** (118.4 mg, 78% yield, 99/96% ee, 65:35 dr)

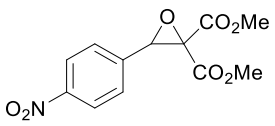


3aa **5a**

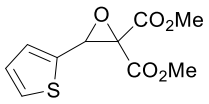
48% yield, 96% ee, >95:5 d.r.

An oven-dried test tube was charged with **3aa** (0.1 mmol, 50.6 mg, 99% ee, >19:1 dr), $AlCl_3$ (1.5 equiv) and CH_2Cl_2 (1.0 mL) under N_2 atmosphere and the resulting solution was stirred at room temperaturet for 5 min. After the reaction was completed, the reaction was quenched with H_2O (3 mL) and washed by saturated $NaHCO_3$, then extracted with CH_2Cl_2 (2×10 mL). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1) to afford the desired product **5a** (24.3. mg, 48% yield, 96% ee, 95:5 dr). Note: The enantioselectivity will drop if longer reaction time (1 hour) was used.

7 Unsuccessful Substrates



NR



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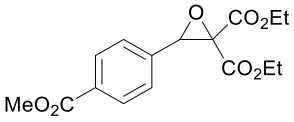

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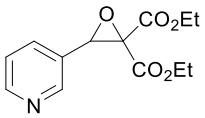

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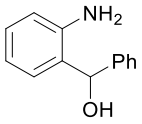

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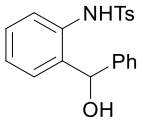

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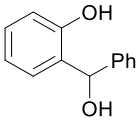

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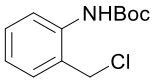

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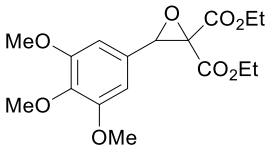

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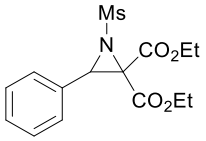

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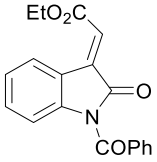

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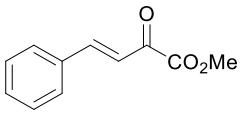

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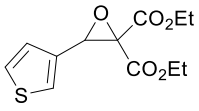

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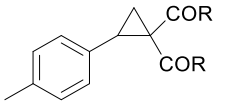
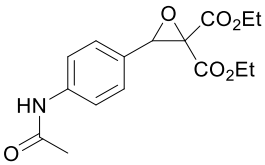
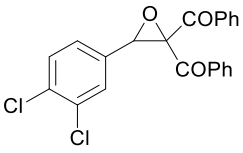


R= OMe or Ph

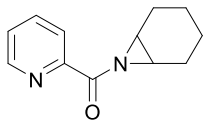
NR



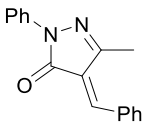
NR



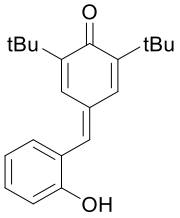
NR



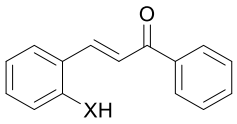
NR



NR

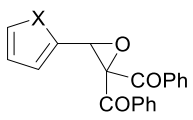


NR



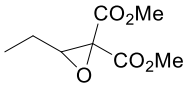
X= NH or O

NR

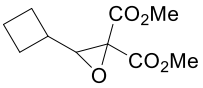


failed

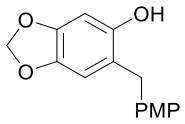
X=O or S



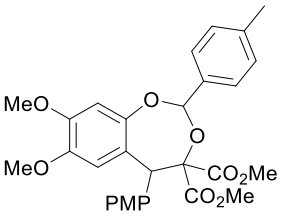
failed



failed



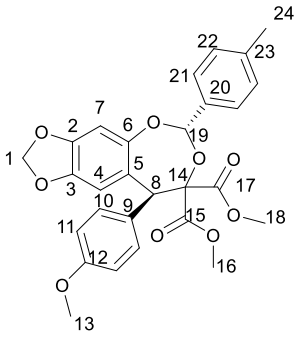
trace



6a

84% yield, 43/76 % ee,
1:1 dr, 48 h

8 Analysis Results of 2D NMR Spectra of the Product 3aa (After Recrystallization)

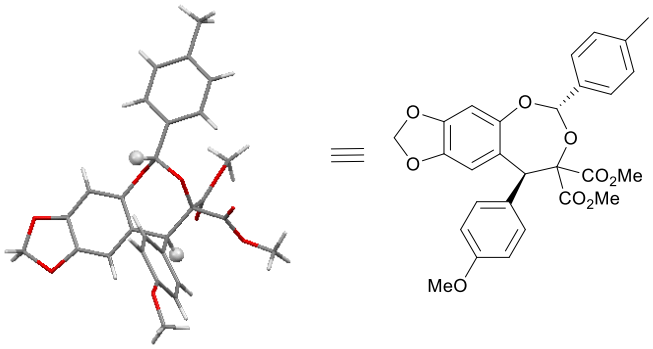


Number of atom	H (ppm)	C (ppm)	Number of atom	H (ppm)	C (ppm)
1	**5.88**	**101.6**	**13**	**3.78**	**55.5**
2	**-**	**144.6**	**14**	**-**	**85.5**
3	**-**	**146.7**	**15**	**-**	**167.6**
4	**6.47**	**110.2**	**16**	**3.59**	**53.0**
5	**-**	**123.7**	**17**	**-**	**169.0**
6	**-**	**151.2**	**18**	**3.68**	**53.0**
7	**6.52**	**101.6**	**19**	**6.25**	**103.9**
8	**5.21**	**53.0**	**20**	**-**	**135.1**
9	**-**	**130.5**	**21**	**7.57**	**126.4**
10	**7.32**	**131.4**	**22**	**7.22**	**129.0**
11	**6.87**	**114.0**	**23**	**-**	**139.0**
12	**-**	**159.0**	**24**	**2.37**	**21.5**

9 Determination of Absolute Configuration and the X-ray Structure of 3aa

The absolute configuration of the optically active product **3aa** was determined to be (2*S*, 6*S*) by X-ray crystal analysis.

The single crystal of **3aa** was obtained from mixed solvents of CH_2Cl_2 and isopropyl alcohol CCDC 1997724 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



the thermal ellipsoid figure of **3aa** with 50% probablities

Crystallographic Data for **3aa.**

Formula	$C_{28}H_{26}O_9$
Formula mass (amu)	506.16
Space group	P 21 21 21

a (Å)	16.395 (3)
c (Å)	17.287 (4)
c (Å)	17.363 (4)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	4920.8(18)
Z	8
λ (Å)	1.54178
T (K)	300 K
ρ_{calcd} (g cm^{-3})	1.367
μ (mm^{-1})	0.857
Transmission factors	0.650-0.754
$2\theta_{max}$ (deg)	74.179
No. of unique data, including $F_o^2 < 0$	9703
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	8938
No. of variables	675
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0338
$R_w(F_o^2)$ [b]	0.0976
Goodness of fit	1.020

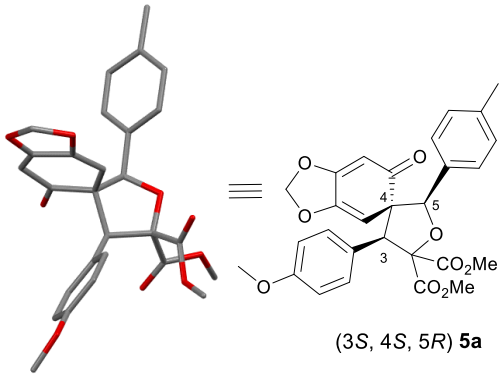
[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

10 Determination of Absolute Configuration and the X-ray Structure of 5a

The absolute configuration of the optically active product **5a** was determined to be (3*S*, 4*S*, 5*R*) by X-ray crystal analysis.

The single crystal of **5a** was obtained from mixed solvents of methanol and petroleum ether CCDC 2026588 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



(3*S*, 4*S*, 5*R*) **5a**

the thermal ellipsoid figure of **5a** with 50% probabilities

Crystallographic Data for **5a.**

Formula	$C_{28}H_{26}O_9$
Formula mass (amu)	506.16
Space group	R 3 :H
a (Å)	28.1257(8)
c (Å)	28.1257(8)
c (Å)	8.1020(3)
α (deg)	90
β (deg)	90
γ (deg)	120
V (Å^3)	5550.5(4)
Z	9
λ (Å)	1.54178
T (K)	144 K
ρ_{calcd} (g cm^{-3})	1.364
μ (mm^{-1})	0.855
Transmission factors	0.658-1.000
$2\theta_{max}$ (deg)	72.408
No. of unique data, including $F_o^2 < 0$	4103
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	3853
No. of variables	339
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0972
$R_w(F_o^2)$ [b]	0.2310
Goodness of fit	1.213

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

11. The dr value determined by ^{1}H NMR and HPLC analysis on a chiral stationary phase.

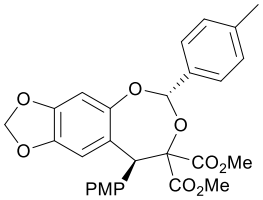
entry[a]	yield (%)[b]	dr (%) (^{1}H NMR)	dr (%) (HPLC)	ee (%)[c]
3aa	99	89:11	89:11	96
3ab	99	91:9	87:13	90
3ac	97	81:19	75:25	88
3ad	99	88:12	84:16	94
3ae	95	84:16	83:17	97
3af	98	90:10	93:7	95
3ag	67	87:13	91:9	74
3ah	71	93:7	91:9	93
3ai	75	86:14	88:12	92
3aj	78	92:8	95:5	96

3ak	55	78:22	81:19	94
3al	37	87:13	83:17	91
3am	67	80:20	81:19	93
3an	51	83:17	86:14	97
3ao	72	88:12	85:15	90
3ap	92	89:11	86:14	84
3aq	53	86:14	83:17	85
3ar	18	89:11	87:13	44
3as	67	94:6	96:4	90
3at	82	89:11	94:6	89
3au	34	89:11	86:14	87
3av	54	91:9	87:13	91
3aw	43	91:9	95:5	93
3ax	51	85:15	84:16	80
3ba	84	94:6	92:8	95
3da	43	94:6	98:2	51
6a	84	50:50	50:50	43/76

[a] Unless otherwise noted, all reactions were carried out with $Tb(OTf)_3$/**L_3-PiPr$_3$** (1:1, 10 mol%), 1a (0.12 mmol) and 2a (0.10 mmol) in DCM (1.0 mL) at 20 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

12 Characterization of the Products

Dimethyl (2*S*,5*S*)-9-(4-methoxyphenyl)-6-(p-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3aa):



89:11 dr, the major diastereomer was isolated as white solid in 93% yield, m.p. = 82–86 °C, 96% ee, $[\alpha]^{18}_D$ = +32.0 (*c* = 0.81, in CH_2Cl_2).

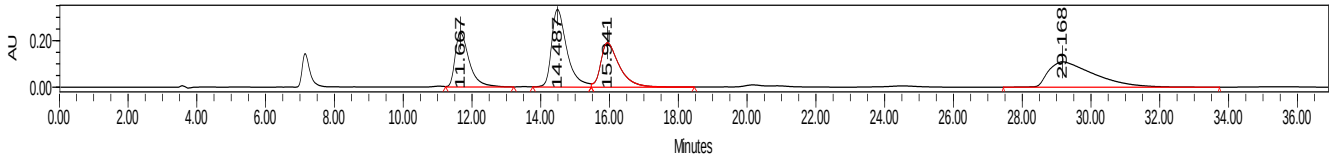
HPLC: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 14.51 min, t_{r2} = 30.52 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 6.54 (s, 1H), 6.48 (s, 1H), 6.26 (s, 1H), 5.89 (s, 2H), 5.22 (s, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.60 (s, 3H), 2.39 (s, 3H).

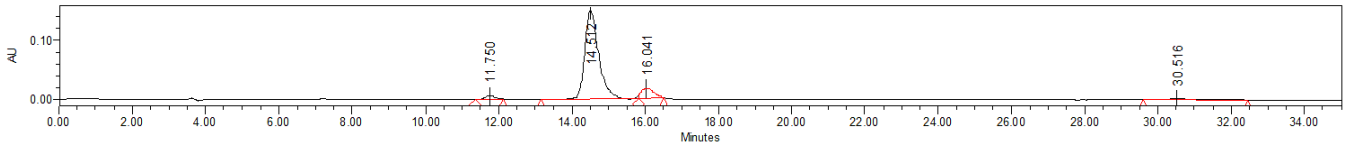
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 167.6, 158.9, 151.2, 146.7, 144.6, 139.0, 135.1, 131.5, 130.4, 129.0, 126.4, 123.7, 114.0, 110.2, 103.9, 101.9, 101.6, 85.5, 55.2, 53.0, 52.9, 52.8, 21.3.

HRMS (ESI) Calculated for $C_{28}H_{26}O_9$ ([M]+Na^+) = 529.1469, Found 529.1459.

IR (neat): 3000, 2952, 2900, 1745, 1610, 1581, 1510, 1480, 1237, 1168, 1033, 935, 881, 862, 838, 804, 733, 549 cm^{-1}.

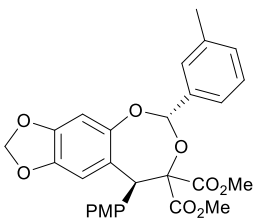


	Retention Time	Area	% Area
1	11.667	6708252	19.57
2	14.487	10364261	30.24
3	15.941	7152558	20.87
4	29.168	10051679	29.33



	Retention Time	Area	% Area
1	11.750	105299	2.31
2	14.512	3961021	86.82
3	16.041	382176	8.38
4	30.516	113945	2.50

Dimethyl (2*S*,5*S*)-9-(4-methoxyphenyl)-6-(m-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ab):



87:13 dr, the major diastereomer was isolated as white solid in 99% yield, m.p. = 64–69 °C, ee = 90%, $[\alpha]^{18}_D$ = +35.2 (*c* = 0.89, in CH_2Cl_2).

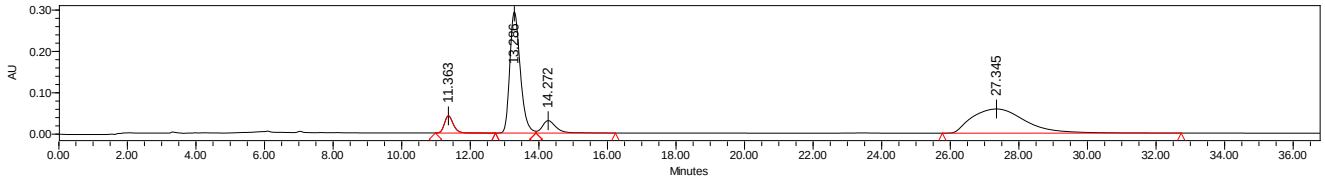
HPLC: Chiralcel IE, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 11.65 min, t_{r2} = 25.64 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.1 Hz, 2H), 7.27 – 7.20 (m, 3H), 7.12 (d, J = 7.7 Hz, 1H), 6.79 (d, J = 9.0 Hz, 2H), 6.47 (s, 1H), 6.40 (s, 1H), 6.16 (s, 1H), 5.81 (s, 2H), 5.14 (s, 1H), 3.71 (s, 3H), 3.61 (s, 3H), 3.53 (s, 3H), 2.32 (s, 3H).

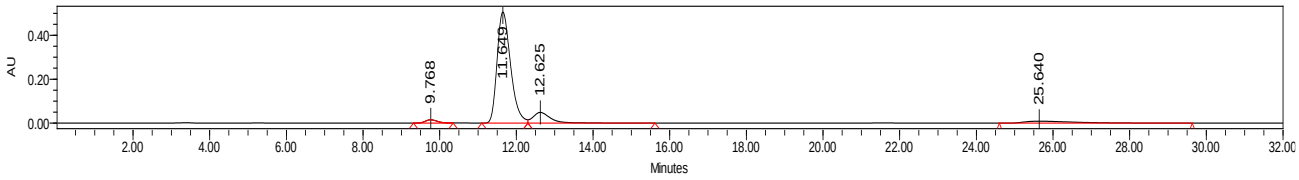
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.9, 166.5, 157.9, 150.2, 145.7, 143.6, 136.9, 136.7, 130.4, 129.4, 128.9, 127.2, 126.0, 122.5, 113.0, 109.1, 102.9, 100.8, 100.6, 84.5, 54.2, 52.0, 51.9, 20.5.

HRMS (ESI) Calculated for $C_{28}H_{26}O_9$ ([M]+Na^+) = 529.1469, Found 529.1967.

IR (neat): 2953, 2904, 1746, 1610, 1581, 1480, 1238, 1172, 1034, 936, 882, 803, 734 cm^{-1}.

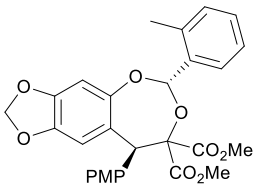


	Retention Time	Area	% Area
1	11.363	753013	5.34
2	13.286	6202824	43.96
3	14.272	839454	5.95
4	27.345	6313702	44.75



	Retention Time	Area	% Area
1	9.768	336104	2.23
2	11.649	12382210	82.02
3	12.625	1573499	10.42
4	25.640	804925	5.33

Dimethyl (2*S*,5*S*)-9-(4-methoxyphenyl)-6-(o-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ac):



75:25 dr, the major diastereomer was isolated as yellow solid in 97% yield, m.p. = 83–88 °C, ee = 88%, $[\alpha]^{20}_D$ = +61.6 (*c* = 0.77, in CH_2Cl_2).

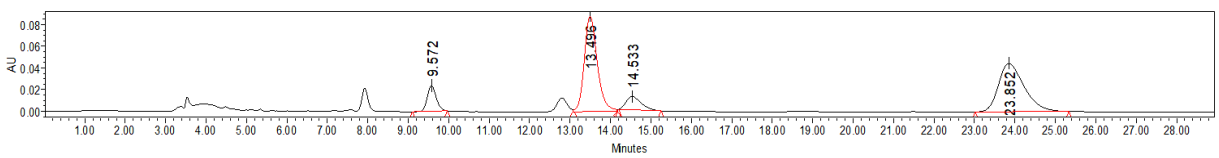
HPLC: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 13.49 min, t_{r2} = 24.01 min.

^1H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 1H), 7.30 – 7.26 (m, 4H), 7.25 (s, 1H), 7.21 – 7.15 (m, 1H), 6.86 (d, J = 8.4 Hz, 2H), 6.54 (s, 1H), 6.49 (d, J = 5.4 Hz, 2H), 5.89 (s, 2H), 5.26 (s, 1H), 3.78 (s, 3H), 3.67 (d, J = 5.7 Hz, 6H), 2.36 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.3, 167.6, 159.0, 151.3, 146.8, 144.6, 135.8, 135.8, 131.2, 130.5, 130.3, 129.2, 126.4, 126.0, 123.1,114.0, 110.1, 102.0, 101.7, 101.6, 85.4, 55.2, 53.1, 53.0, 52.4, 19.4.

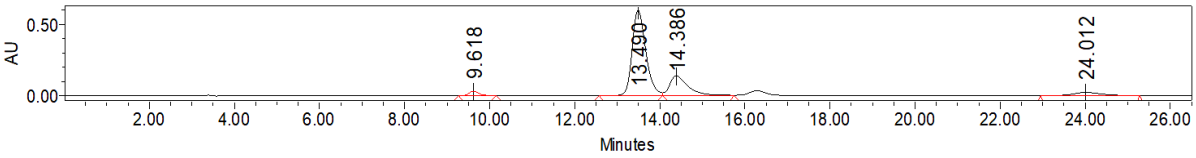
HRMS (ESI) Calculated for $C_{28}H_{26}O_9$ ([M]+H^+) = 529.1469, Found 529.1472.

IR (neat): 2935, 2903, 1746, 1610, 1582, 1510, 1480, 1238, 1171, 1035, 993, 937, 869, 838, 806, 756, 734 cm^{-1}.



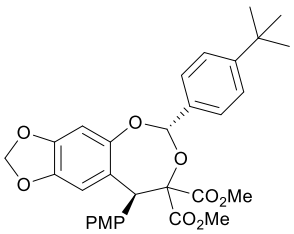
	Retention Time	Area	% Area
1	9.572	363930	7.90
2	13.496	1968272	42.75
3	14.533	315849	6.86

4	23.852	1956153	42.49



	Retention Time	Area	% Area
1	9.618	511124	2.68
2	13.490	13377267	70.13
3	14.386	4177215	21.90
4	24.012	1008107	5.29

Dimethyl (2*S*,5*S*)-6-(4-(tert-butyl)phenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ad):



84:16, the major diastereomer was isolated as colorless solid in 99% yield, m.p. = 94–98 °C, ee = 94%, $[\alpha]^{19}_D$ = +26.5 (*c* = 0.62, in CH_2Cl_2).

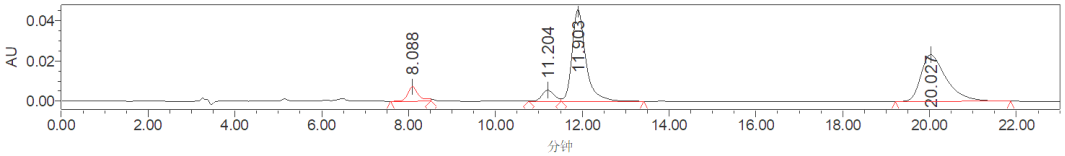
HPLC: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 11.71 min, t_{r2} = 19.89 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 6.54 (s, 1H), 6.50 (s, 1H), 6.25 (s, 1H), 5.89 (s, 2H), 5.22 (s, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.61 (s, 3H), 1.34 (s, 9H).

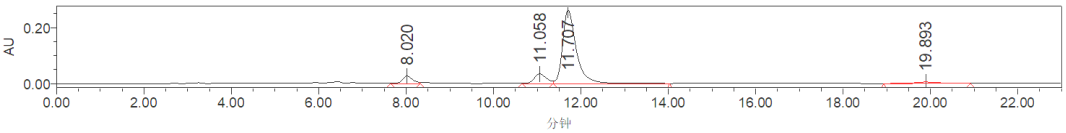
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 167.7, 158.9, 152.2, 151.3, 146.7, 144.6, 135.0, 131.5, 130.4, 126.2, 125.3, 123.7, 114.0, 110.2, 103.9, 101.8, 101.6, 85.6, 55.2, 53.0, 52.9, 34.7, 31.4.

HRMS (ESI) Calculated for $C_{31}H_{32}O_9$ ([M+Na$^+$]) = 571.1938, Found 571.1937.

IR (neat): 2955, 2904, 1749, 1610, 1511, 1481, 1241, 1172, 1037, 938, 869, 823, 804 cm^{-1}.

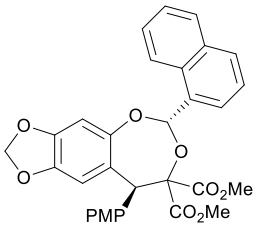


	Retention Time	Area	% Area
1	8.088	127269	5.85
2	11.204	109126	5.02
3	11.903	996516	45.80
4	20.027	942679	43.33



	Retention Time	Area	% Area
1	8.020	440675	6.30
2	11.058	662862	9.48
3	11.707	5668244	81.05
4	19.893	221559	3.17

Dimethyl (2*S*,5*S*)-9-(4-methoxyphenyl)-6-(naphthalen-1-yl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ae):



83:17 dr, the major diastereomer was isolated as yellow solid in 95% yield, m.p. = 107–115 °C, ee = 97%, $[\alpha]^{19}_D$ = +70.9 (c = 0.74, in CH_2Cl_2).

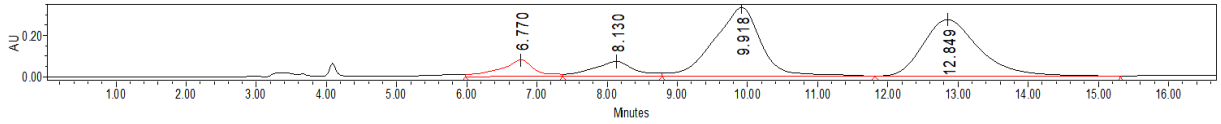
HPLC: Chiralcel IC, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 10.20 min, t_{r2} = 12.99 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.1 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.57 – 7.50 (m, 3H), 7.34 (d, J = 8.2 Hz, 2H), 7.06 (s, 1H), 6.87 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 3.5 Hz, 2H), 5.92 (d, J = 8.8 Hz, 2H), 5.33 (s, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H).

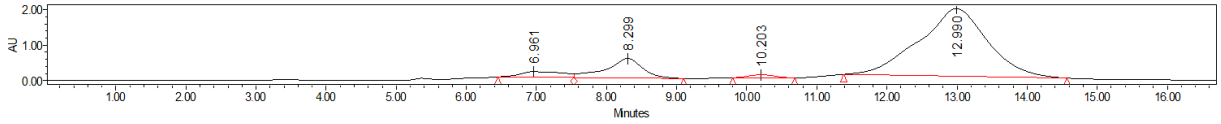
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.3, 167.6, 159.0, 151.1, 146.9, 144.9, 133.7, 132.8, 131.3, 129.9, 128.9, 126.5, 125.6, 125.3, 124.8, 123.5, 123.3, 114.1, 110.3, 102.1, 101.9, 101.7, 85.5, 55.2, 53.1, 53.0, 52.5.

HRMS (ESI) Calculated for $C_{31}H_{26}O_9$ ([M+Na$^+$]) = 565.1469, Found 565.1476.

IR (neat): 3056, 3009, 2902, 1747, 1610, 1511, 1481, 1238, 1177, 1037, 993, 938, 890, 873, 821, 797, 734 cm^{-1}.

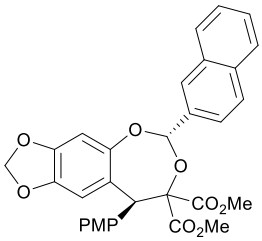


	Retention Time	Area	% Area
1	6.770	2731592	7.50
2	8.130	3027411	8.31
3	9.918	15549573	42.69
4	12.849	15114429	41.50



	Retention Time	Area	% Area
1	6.961	6718260	4.26
2	8.299	19801222	12.56
3	10.203	2140426	1.36
4	12.990	129040310	81.83

Dimethyl (2*S*,5*S*)-9-(4-methoxyphenyl)-6-(naphthalen-2-yl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3af):



93:7 dr, the major diastereomer was isolated as white solid in 98 yield, m.p. = 102–107 °C , ee = 95%, $[\alpha]^{27}_D$ = +9.6 (*c* = 1.00, in CH_2Cl_2).

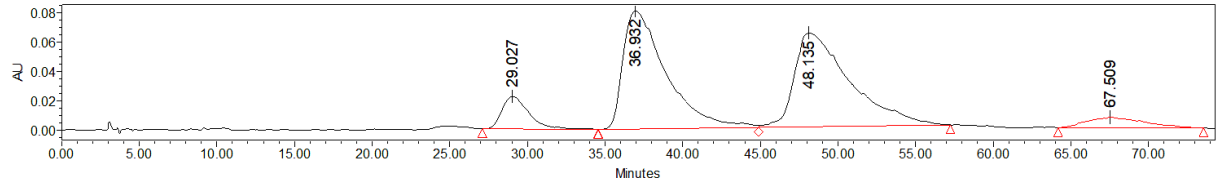
HPLC: Chiralcel ODH, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 36.52 min, t_{r2} = 51.64 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.90 (dd, J = 8.9, 4.0 Hz, 2H), 7.85 (dd, J = 6.5, 3.0 Hz, 1H), 7.78 (dd, J = 8.5, 1.7 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.35 (d, J = 8.2 Hz, 2H), 6.92 – 6.86 (m, 2H), 6.59 (s, 1H), 6.50 (s, 1H), 6.45 (s, 1H), 5.89 (s, 2H), 5.26 (s, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.59 (s, 3H).

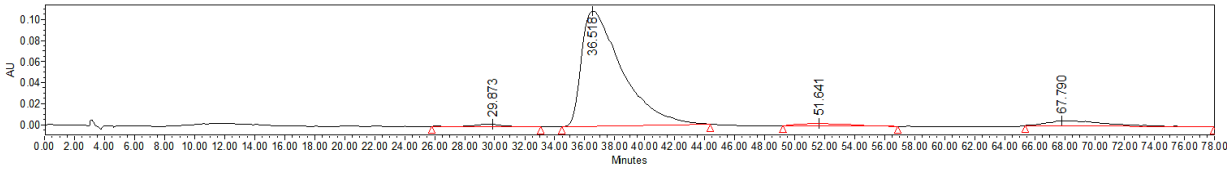
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 167.6, 159.0, 151.2, 146.8, 144.7, 135.2, 133.7, 132.9, 131.5, 130.5, 128.5, 128.2, 127.7, 126.5, 126.2, 126.0, 124.0, 123.7, 114.1, 110.2, 103.9, 101.9, 101.6, 85.6, 55.2, 53.1, 53.0, 52.9.

HRMS (ESI) Calculated for $C_{31}H_{26}O_9$ ([M+Na$^+$]) = 565.1469, Found 565.1467.

IR (neat): 2953, 2902, 1747, 1610, 1510, 1481, 1239, 1176, 1036, 937, 882, 863, 804, 735 cm^{-1}.

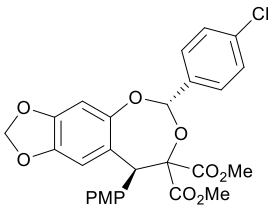


	Retention Time	Area	% Area
1	29.027	2670714	7.47
2	36.932	15472955	43.25
3	48.135	15828668	44.24
4	67.509	1803934	5.04



	Retention Time	Area	% Area
1	29.873	280363	1.24
2	36.518	20551369	91.03
3	51.641	444339	1.97
4	67.790	1299373	5.76

Dimethyl (2*S*,5*S*)-6-(4-chlorophenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ag):



91:9 dr, the major diastereomer was isolated as colorless oil in 67% yield, ee = 74%, $[\alpha]^{27}_{D}$ = +23.6 (*c* = 0.17, in CH_2Cl_2).

HPLC: Chiralcel IB, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 225 nm, t_{r1} = 13.12 min, t_{r2} = 15.36 min.

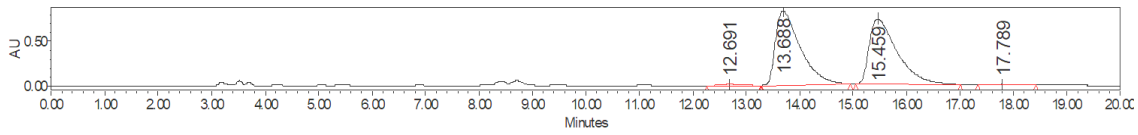
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 6.53 (s, 1H), 6.47 (d, J = 0.7 Hz, 1H), 6.26 (s, 1H), 5.90 (s, 2H), 5.21 (s, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.58 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ168.8, 167.4, 159.0, 150.9, 146.8, 144.8, 136.4, 135.0, 131.4, 130.3, 128.5, 128.0, 123.6, 114.0, 110.2, 103.0, 101.8, 101.7, 85.5, 55.2, 53.1, 52.9.

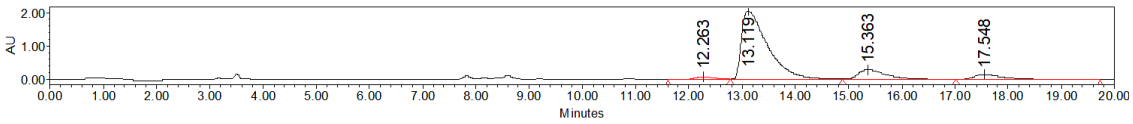
HRMS (ESI) Calculated for $C_{27}H_{23}^{34.9689}ClO_9$ ([M]+Na$^+$) = 549.0923, Found 549.0925.

HRMS (ESI) Calculated for $C_{27}H_{23}^{36.9659}ClO_9$ ([M]+Na$^+$) = 551.0893, Found 551.0903.

IR (neat): 2954, 1749, 1610, 1511, 1481, 1434, 1348, 1240, 1172, 1037, 937, 911, 732 cm^{-1}.

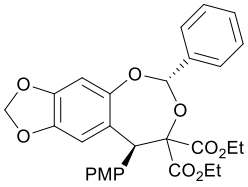


	Retention Time	Area	% Area
1	12.691	393030	0.72
2	13.688	27025336	49.61
3	15.459	26797159	49.19
4	17.789	258121	0.47



	Retention Time	Area	% Area
1	12.263	2467841	2.72
2	13.119	70774946	77.94
3	15.363	11462555	12.62
4	17.548	6095836	6.71

Diethyl (2*S*,5*S*)-9-(4-methoxyphenyl)-6-phenyl-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate(3ah):



91:9 dr, the major diastereomer was isolated as colorless oil in 71% yield, ee = 93%, $[\alpha]^{19}_D$ = +34.6 (*c* = 0.32, in CH_2Cl_2).

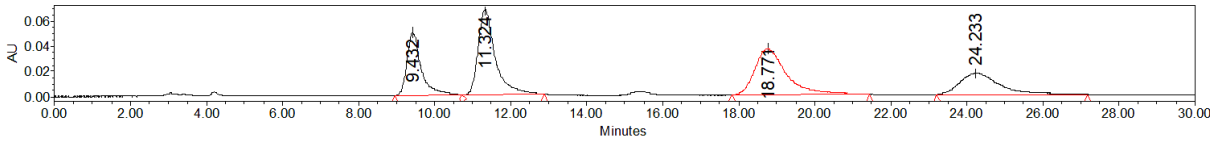
HPLC: Chiralcel ADH, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 225 nm, t_{r1} = 11.58 min, t_{r2} = 19.30 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.44 – 7.34 (m, 5H), 6.88 – 6.85 (m, 2H), 6.56 (s, 1H), 6.48 (s, 1H), 6.24 (s, 1H), 5.89 (s, 2H), 5.21 (s, 1H), 4.18 (qd, *J* = 7.1, 1.4 Hz, 2H), 4.09 – 4.00 (m, 2H), 3.79 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).

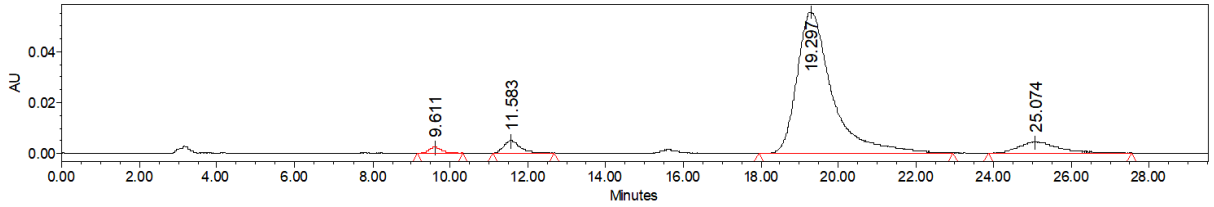
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.3, 167.0, 158.9, 151.2, 146.6, 144.6, 138.1, 131.7, 130.5, 129.0, 128.2, 126.6, 113.9, 110.2, 103.6, 101.8, 101.6, 85.4, 62.1, 62.1, 55.2, 52.9, 14.0, 13.6.

HRMS (ESI) Calculated for $C_{29}H_{28}O_9$ ([M]+Na^+) = 543.1625, Found 543.1624.

IR (neat): 2981, 2915, 1744, 1610, 1511, 1481, 1368, 1302, 1239, 1173, 1037, 933, 862, 838, 803, 748, 698 cm^{-1}.

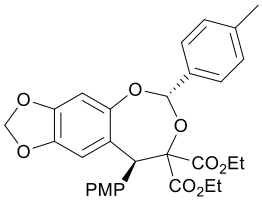


	Retention Time	Area	% Area
1	9.432	1326922	19.40
2	11.324	2140011	31.29
3	18.771	2141331	31.31
4	24.233	1230286	17.99



	Retention Time	Area	% Area
1	9.611	57470	1.44
2	11.583	152038	3.81
3	19.297	3456499	86.73
4	25.074	319284	8.01

Diethyl (2*S*,5*S*)-9-(4-methoxyphenyl)-6-(p-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate(3ai):



88:12 dr, the major diastereomer was isolated as white solid in 75% yield, m.p. = 63–71 °C, ee = 92%, $[\alpha]^{19}_D$ = +28.2 (*c* = 0.83, in CH_2Cl_2).

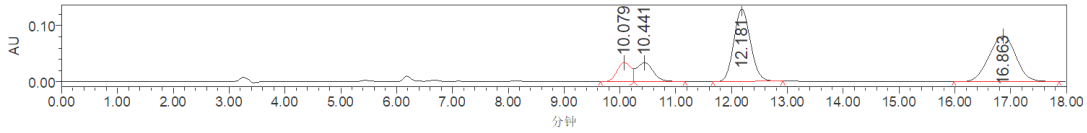
HPLC: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 11.85 min, t_{r2} = 16.53 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.7 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 6.85 (d, J = 8.3 Hz, 2H), 6.53 (s, 1H), 6.47 (s, 1H), 6.19 (s, 1H), 5.88 (s, 2H), 5.20 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.04 (ddd, J = 10.2, 7.0, 2.7 Hz, 2H), 3.79 (s, 3H), 2.38 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H).

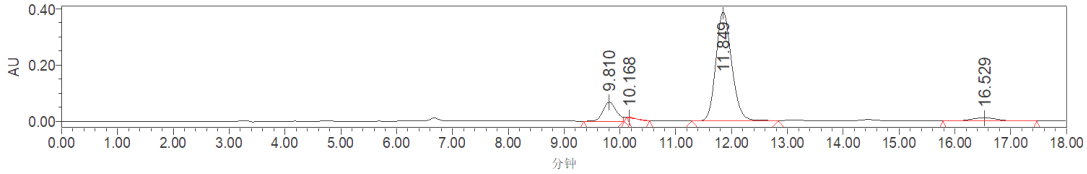
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.3, 167.1, 158.9, 151.3, 146.6, 144.5, 138.9, 135.3, 131.7, 130.5, 128.9, 126.5, 124.2, 113.9, 110.2, 103.7, 101.8, 101.5, 85.4, 62.1, 62.0, 55.2, 52.9, 21.3, 14.0, 13.6.

HRMS (ESI) Calculated for $C_{30}H_{30}O_9$ ([M+Na$^+$]) = 557.1782, Found 557.1780.

IR (neat): 2981, 2902, 1742, 1610, 1582, 1479, 1238, 1170, 1035, 991, 933, 862, 837, 804, 735, 698 cm^{-1}.

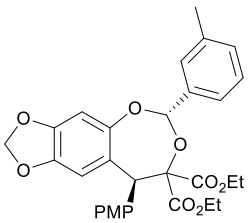


	Retention Time	Area	% Area
1	10.079	593201	8.88
2	10.441	692816	10.37
3	12.181	2657583	39.78
4	16.863	2736968	40.97



	Retention Time	Area	% Area
1	9.810	1103700	11.96
2	10.168	33958	0.37
3	11.849	7706952	83.53
4	16.529	381971	4.14

Diethyl (2*S*,5*S*)-9-(4-methoxyphenyl)-6-(m-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3aj):



95:5 dr, the major diastereomer was isolated as white solid in 78% yield, m.p. = 57–62 °C, ee = 96%, $[\alpha]^{18}_D$ = +32.9 (*c* = 0.47, in CH_2Cl_2).

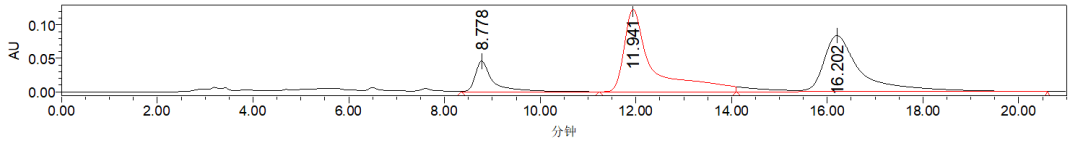
HPLC: Chiralcel ADH, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 11.86 min, t_{r2} = 16.08 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 6.87 (d, J = 9.0 Hz, 2H), 6.56 (s, 1H), 6.48 (s, 1H), 6.20 (s, 1H), 5.89 (s, 2H), 5.21 (s, 1H), 4.21 – 4.15 (m, 2H), 4.06 (tdd, J = 10.7, 7.7, 3.6 Hz, 2H), 3.79 (s, 3H), 2.41 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.1 Hz, 3H).

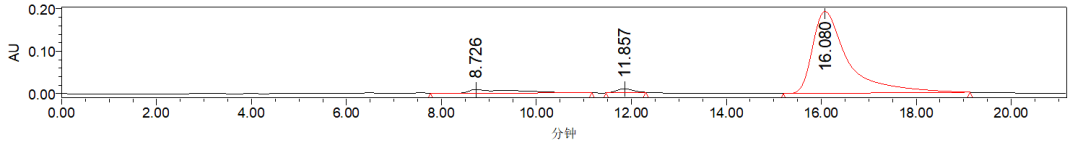
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.3, 167.1, 158.9, 151.3, 146.6, 144.5, 137.9, 131.7, 129.8, 128.1, 127.2, 124.2, 123.7, 113.9, 110.2, 103.7, 101.8, 101.6, 85.5, 62.1, 55.2, 52.9, 21.5, 14.0, 13.6.

HRMS (ESI) Calculated for $C_{30}H_{30}O_9$ ([M+Na$^+$]) = 557.1782, Found 557.1780.

IR (neat): 2981, 2934, 1742, 1610, 1582, 1480, 1444, 1238, 986, 934, 882, 864, 837, 801, 780, 734 cm^{-1}.

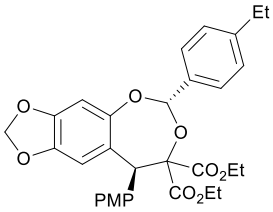


	Retention Time	Area	% Area
1	8.778	1200364	10.83
2	11.941	5076198	45.80
3	16.202	4806342	43.37



	Retention Time	Area	% Area
1	8.726	623618	5.73
2	11.857	216729	1.99
3	16.080	10041116	92.28

Diethyl (2*S*,5*S*)-6-(4-ethylphenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ak):



81:19 dr, the major diastereomer was isolated as yellow oil in 55% yield, ee = 94%, $[\alpha]^{18}_{D}$ = +23.8 (*c* = 0.51, in CH_2Cl_2).

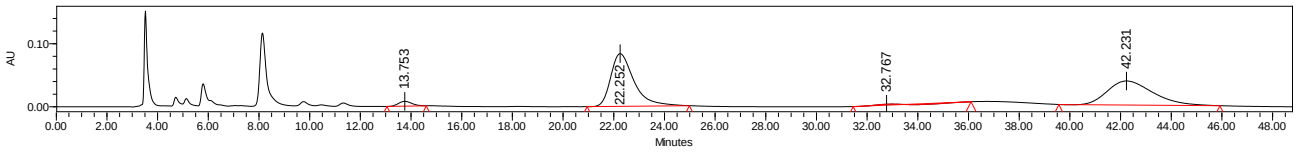
HPLC: Chiralcel ADH, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 21.84 min, t_{r2} = 40.82 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.26 – 7.24 (m, 2H), 6.86 (d, *J* = 9.1 Hz, 2H), 6.54 (s, 1H), 6.48 (d, *J* = 0.6 Hz, 1H), 6.21 (s, 1H), 5.88 (s, 2H), 5.21 (s, 1H), 4.17 (qd, *J* = 7.1, 1.2 Hz, 2H), 4.08 – 4.02 (m, 2H), 3.79 (s, 3H), 2.70 – 2.66 (m, 2H), 1.25 (d, *J* = 7.6 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).

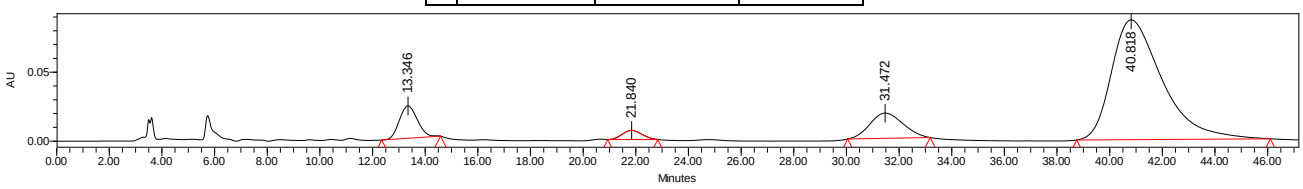
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.3, 167.1, 158.9, 151.3, 146.6, 145.3, 144.5, 135.5, 131.7, 130.5, 127.7, 126.6, 124.2, 113.9, 110.2, 103.7, 101.9, 101.5, 85.4, 62.1, 62.0, 55.2, 52.9, 28.7, 15.7, 14.0, 13.6.

HRMS (ESI) Calculated for $C_{31}H_{32}O_9$ ([M]+Na^+) = 585.2095, Found 585.2100.

IR (neat): 2963, 2904, 1743, 1611, 1510, 1480, 1239, 1171, 1037, 991, 936, 863, 834, 805 cm^{-1}.

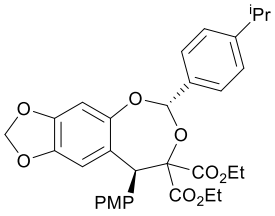


	Retention Time	Area	% Area
1	13.753	284149	2.69
2	22.252	5323642	50.34
3	32.767	193368	1.83
4	42.231	4775098	45.15



	Retention Time	Area	% Area
1	13.346	1116946	7.61
2	21.840	342058	2.33
3	31.472	1603364	10.92
4	40.818	11623348	79.15

Diethyl (2*S*,5*S*)-6-(4-isopropylphenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3al):



83:17 dr, the major diastereomer was isolated as white solid in 37% yield, m.p. = 58–64 °C, ee = 91%, $[\alpha]^{18}_D$ = +23.3 (*c* = 0.50, in CH_2Cl_2).

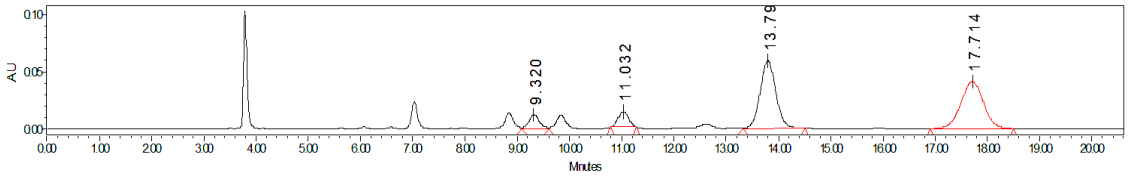
HPLC: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 14.13 min, t_{r2} = 18.26 min.

1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.29 – 7.25 (m, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.53 (s, 1H), 6.47 (s, 1H), 6.18 (s, 1H), 5.88 (s, 2H), 5.20 (s, 1H), 4.87 (s, 0H), 4.16 (q, J = 7.1 Hz, 2H), 4.04 (dp, J = 9.1, 6.8, 5.2 Hz, 2H), 3.79 (s, 3H), 2.97 – 2.89 (m, 1H), 1.26 (d, J = 6.9 Hz, 6H), 1.18 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H).

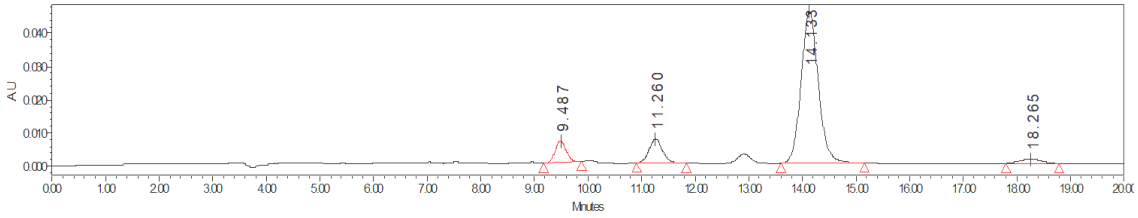
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.1, 158.9, 151.3, 149.9, 146.6, 144.5, 135.6, 131.7, 130.5, 128.0, 126.6, 126.3, 124.2, 113.9, 110.2, 103.7, 101.8, 101.5, 85.5, 62.1, 62.0, 55.2, 52.9, 34.0, 24.0, 14.0, 13.6.

HRMS (ESI) Calculated for $C_{32}H_{34}O_9$ ([M]+H^+) = 563.2275, Found 563.2280.

IR (neat): 2960, 2903, 1741, 1611, 1510, 1480, 1238, 1170, 1035, 990, 936, 862, 832, 805, 735 cm^{-1}.

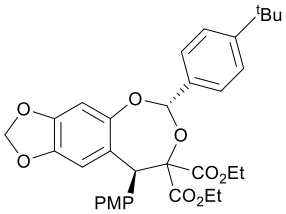


	Retention Time	Area	% Area
1	9.320	172056	6.03
2	11.032	194753	6.83
3	13.798	1242178	43.54
4	17.714	1243843	43.60



	Retention Time	Area	% Area
1	9.487	94290	7.39
2	11.260	125262	9.82
3	14.133	1018765	79.84
4	18.265	37734	2.96

Diethyl (2*S*,5*S*)-6-(4-(tert-butyl)phenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3am):



81:19 dr, the major diastereomer was isolated as colorless oil in 67% yield, ee = 93%, $[\alpha]^{18}_D$ = +16.9 (*c* = 0.57, in CH_2Cl_2).

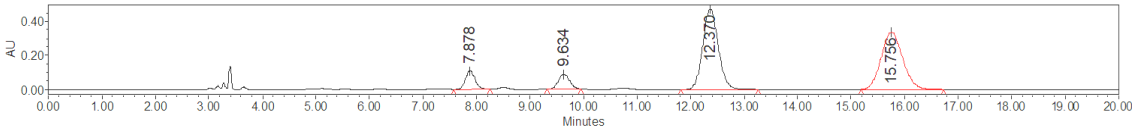
HPLC: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm, t_{r1} = 12.39 min, t_{r2} = 15.84 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.35 (m, 2H), 6.88 – 6.85 (m, 2H), 6.54 (s, 1H), 6.49 (s, 1H), 6.20 (s, 1H), 5.89 (s, 2H), 5.21 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.08 – 4.02 (m, 2H), 3.79 (s, 3H), 1.35 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).

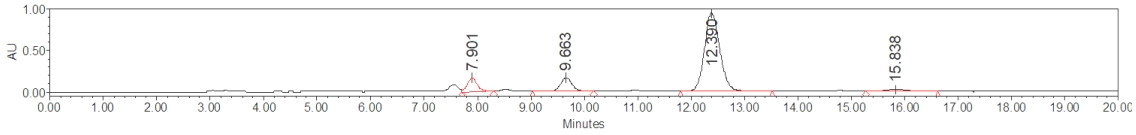
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.3, 167.1, 158.9, 152.1, 151.3, 146.5, 144.5, 135.2, 131.7, 130.5, 126.3, 125.2, 124.2, 113.9, 110.2, 103.6, 101.8, 101.5, 85.5, 62.1, 62.0, 55.2, 52.9, 34.7, 31.4, 14.0, 13.6.

HRMS (ESI) Calculated for $C_{33}H_{36}O_9$ ([M+Na$^+$]) = 599.2251, Found 599.2252.

IR (neat): 2961, 2904, 1743, 1611, 1510, 1480, 1238, 1170, 1035, 990, 936, 862, 835, 803,735, 561 cm^{-1}.

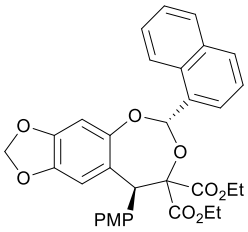


	Retention Time	Area	% Area
1	7.878	1370388	6.32
2	9.634	1309606	6.04
3	12.370	9591440	44.26
4	15.756	9401284	43.38



	Retention Time	Area	% Area
1	7.901	2162591	8.74
2	9.663	2616432	10.57
3	12.390	19190246	77.55
4	15.838	775660	3.13

Diethyl (2*S*,5*S*)-9-(4-methoxyphenyl)-6-(naphthalen-1-yl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3an):



86:14 dr, the major diastereomer was isolated as colorless oil in 51% yield, ee = 97%, $[\alpha]^{18}_D$ = +28.3 (*c* = 0.33, in CH_2Cl_2).

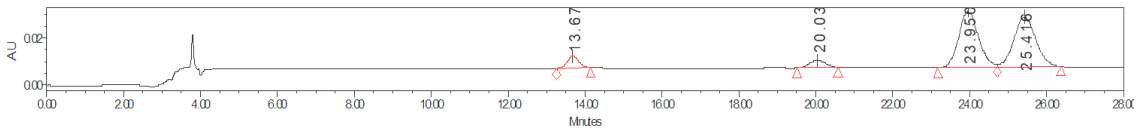
HPLC: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 23.97 min, t_{r2} = 25.54 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.2 Hz, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.92 – 7.91 (m, 1H), 7.90 – 7.88 (m, 1H), 7.52 (dd, J = 8.8, 7.1 Hz, 3H), 7.38 (d, J = 8.2 Hz, 2H), 7.03 (s, 1H), 6.88 (d, J = 1.7 Hz, 1H), 6.86 (s, 1H), 6.55 (d, J = 1.1 Hz, 2H), 5.93 (d, J = 1.4 Hz, 1H), 5.91 (d, J = 1.4 Hz, 1H), 5.32 (s, 1H), 4.23 – 4.17 (m, 2H), 4.11 (t, J = 7.1 Hz, 2H), 3.78 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.08 (q, J = 3.7 Hz, 3H).

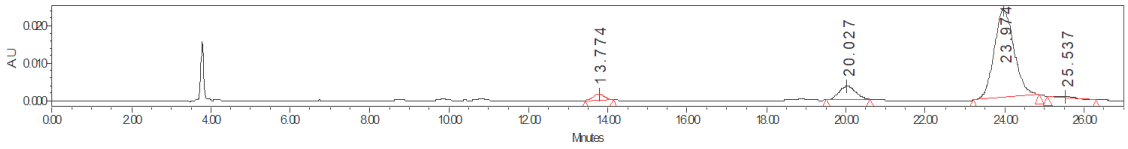
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.9, 167.1, 159.0, 151.1, 146.7, 144.7, 133.7, 132.9, 131.5, 130.7, 130.6, 129.9, 128.9, 126.4, 125.6, 125.2, 125.1, 123.5, 114.0, 110.3, 102.2, 101.9, 101.6, 85.3, 62.3, 62.1, 55.3, 14.0, 13.8.

HRMS (ESI) Calculated for $C_{33}H_{30}O_9$ ([M+Na$^+$]) = 593.1782, Found 593.1774.

IR (neat): 2981, 2905, 1743, 1611, 1510, 1481, 1241, 1174, 1036, 988, 935, 865, 836, 806, 735 cm^{-1}.

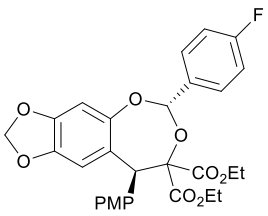


	Retention Time	Area	% Area
1	13.673	128174	6.61
2	20.032	99292	5.12
3	23.950	861421	44.42
4	25.416	850444	43.85



	Retention Time	Area	% Area
1	13.774	32065	3.32
2	20.027	106860	11.06
3	23.974	816038	84.49
4	25.537	10888	1.13

Diethyl (2*S*,5*S*)-6-(4-fluorophenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ao):



85:15 dr, the major diastereomer was isolated as colorless oil in 72% yield, ee = 90%, $[\alpha]^{18}_{D}$ = +32.9 (*c* = 0.47, in CH_2Cl_2).

HPLC: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 10.07 min, t_{r2} = 14.11 min.

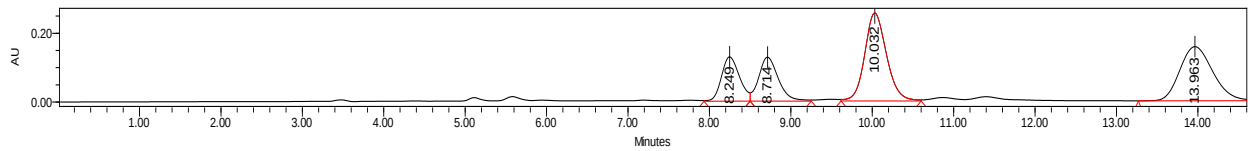
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 8.6, 5.6 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.10 (t, J = 8.7 Hz, 2H), 6.88 – 6.84 (m, 2H), 6.53 (s, 1H), 6.47 (s, 1H), 6.23 (s, 1H), 5.89 (s, 2H), 5.20 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 4.05 (ddd, J = 11.1, 7.2, 3.7 Hz, 2H), 3.79 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.2, 166.9, 164.4 (d, J = 245.7 Hz), 161.9, 159.0, 151.0, 146.6, 144.7, 134.1 (d, J = 3.3 Hz), 131.6, 130.4, 128.5 (d, J = 8.3 Hz), 124.1, 115.2 (d, J = 21.6 Hz), 113.9, 113.8, 110.2, 103.0, 101.8 (d, J = 16.0 Hz), 101.6, 85.4, 62.2, 62.1, 55.2, 52.8, 14.0, 13.6.

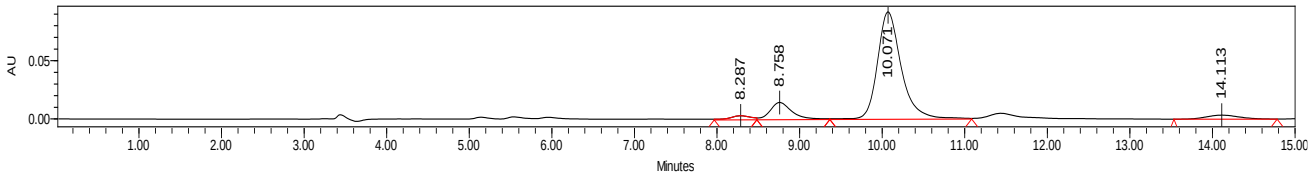
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –112.9 (s, 1F).

HRMS (ESI) Calculated for $C_{29}H_{27}FO_9$ ([M]+H$^+$) = 539.1711, Found 539.1716.

IR (neat): 2982, 2961, 1742, 1609, 1583, 1480, 1237, 1172, 993, 936, 862, 836, 803, 734, 590 cm^{-1}.

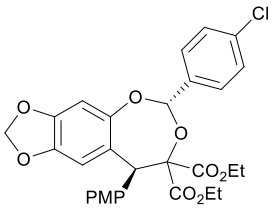


	Retention Time	Area	% Area
1	8.249	1975939	14.85
2	8.714	2142742	16.10
3	10.032	4761492	35.79
4	13.963	4425559	33.26



	Retention Time	Area	% Area
1	8.287	63608	2.77
2	8.758	277574	12.10
3	10.071	1855013	80.87
4	14.113	97559	4.25

Diethyl (2*S*,5*S*)-6-(4-chlorophenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ap):



86:14 dr, the major diastereomer was isolated as colorless oil in 92% yield, ee = 84%, $[\alpha]^{18}_{D}$ = +24.9 (*c* = 0.42, in CH_2Cl_2).

HPLC: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 29.18 min, t_{r2} = 55.09 min.

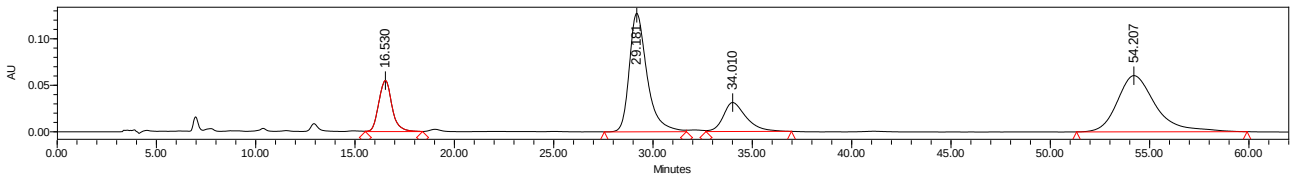
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.53 (s, 1H), 6.46 (s, 1H), 6.22 (s, 1H), 5.89 (s, 2H), 5.19 (s, 1H), 4.17 (q, J = 7.6, 6.7 Hz, 2H), 4.08 – 4.00 (m, 2H), 3.79 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.2, 166.8 , 159.0, 150.9, 146.7, 144.7, 136.6, 134.9, 131.6, 130.4, 128.4, 128.1, 124.1, 113.9, 102.8, 101.7, 101.6, 85.4, 62.2, 62.1, 55.2, 52.8, 14.0, 13.6.

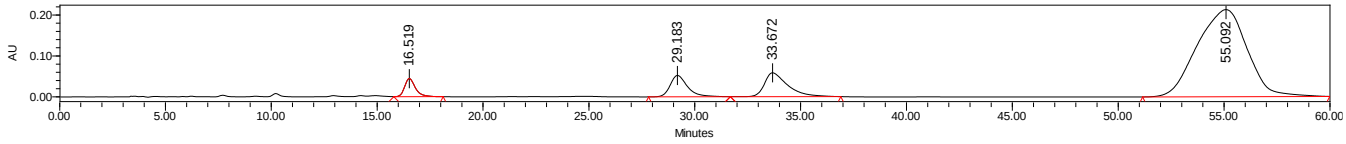
HRMS (ESI) Calculated for $C_{29}H_{27}{}^{34.9689}ClO_9$ ([M]+Na$^+$) = 577.1235, Found 577.1228.

HRMS (ESI) Calculated for $C_{17}H_{19}{}^{36.9659}ClO_5$ ([M]+Na$^+$) = 579.1206, Found 579.1207.

IR (neat): 2981, 2935, 2903, 1743, 1610, 1510, 1480, 1239, 1170, 1036, 936, 863, 835, 818, 735, 544 cm^{-1}.

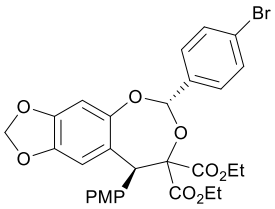


	Retention Time	Area	% Area
1	16.530	2544380	12.10
2	29.181	7899043	37.57
3	34.010	2500916	11.89
4	54.207	8081347	38.44



	Retention Time	Area	% Area
1	16.519	1565057	3.56
2	29.183	2996818	6.82
3	33.672	4468452	10.16
4	55.092	34940201	79.46

Diethyl (2*S*,5*S*)-6-(4-bromophenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3aq):



83:17 dr, the major diastereomer was isolated as yellow oil in 53% yield, ee = 85%, $[\alpha]^{18}_D$ = +11.1 (*c* = 0.33, in CH_2Cl_2).

HPLC: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 225 nm, t_{r1} = 13.42 min, t_{r2} = 19.97 min.

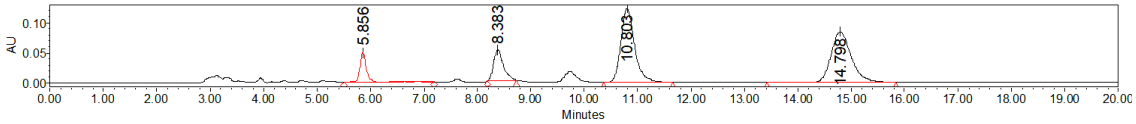
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.89 – 6.84 (m, 2H), 6.53 (s, 1H), 6.46 (s, 1H), 6.20 (s, 1H), 5.89 (s, 2H), 5.19 (s, 1H), 4.17 (qd, J = 7.1, 1.4 Hz, 2H), 4.07 – 4.00 (m, 2H), 3.79 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.2, 166.8, 159.0, 150.9, 146.7, 144.7, 137.1, 131.6, 131.3, 128.4, 124.1, 123.2, 113.9, 110.2, 102.8, 101.7, 101.6, 85.4, 62.2, 62.1, 55.2, 52.8, 14.0, 13.6.

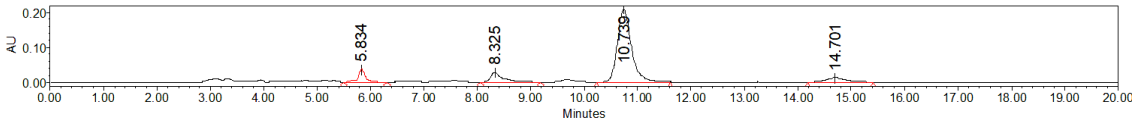
HRMS (ESI) Calculated for $C_{29}H_{27}^{78.9183}BrO_9$ ([M]+Na^+) = 621.0730, Found 621.0732.

HRMS (ESI) Calculated for $C_{29}H_{27}^{80.9163}BrO_9$ ([M]+Na^+) = 623.0710, Found 623.0717.

IR (neat): 2960, 2919, 1744, 1610, 1510, 1480, 1247, 1172, 1036, 936, 863, 836, 813 cm^{-1}.

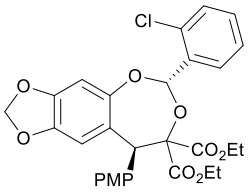


	Retention Time	Area	% Area
1	5.856	439821	7.42
2	8.383	799926	13.50
3	10.803	2200657	37.15
4	14.798	2181878	36.83



	Retention Time	Area	% Area
1	5.834	347831	7.11
2	8.325	441844	9.03
3	10.739	3711290	75.87
4	14.701	296677	6.07

Diethyl (2*S*,5*S*)-6-(2-chlorophenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ar):



87:13 dr, the major diastereomer was isolated as colorless oil in 18% yield, ee = 44%, $[\alpha]^{18}_D$ = +35.0 (*c* = 0.16, in CH_2Cl_2).

HPLC: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 9.78 min, t_{r2} = 11.86 min.

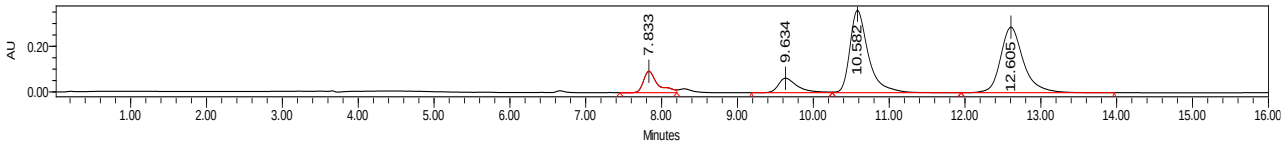
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 9.5 Hz, 1H), 7.45 – 7.27 (m, 5H), 6.86 (d, J = 8.9 Hz, 2H), 6.69 (s, 1H), 6.60 (s, 1H), 6.46 (s, 1H), 5.90 (s, 2H), 5.24 (s, 1H), 4.24 – 4.06 (m, 4H), 3.78 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.8, 159.0, 151.2, 146.5, 144.7, 135.2, 133.3, 131.4, 130.4, 129.2, 129.0, 126.7, 123.4, 114.0, 109.8, 102.2, 101.6, 85.1, 62.3, 62.2, 55.2, 52.2, 14.0, 13.8.

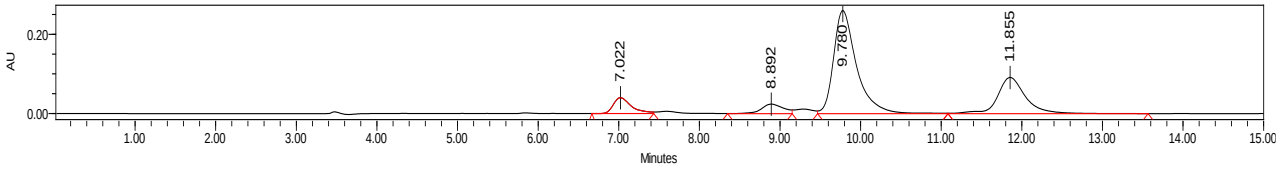
HRMS (ESI) Calculated for $C_{29}H_{27}^{34.9689}ClO_9$ ([M]+Na^+) = 577.1236, Found 577.1230.

HRMS (ESI) Calculated for $C_{17}H_{19}{}^{36.9659}ClO_5$ ([M]+Na$^+$) = 579.1206, Found 579.1212.

IR (neat): 2958, 2924, 1747, 1610, 1511, 1481, 1248, 1174, 1036, 993, 937, 863, 837, 804, 729 cm^{-1}.

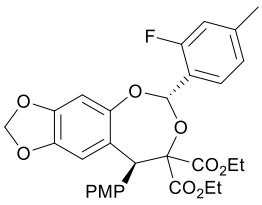


	Retention Time	Area	% Area
1	7.833	1239342	8.57
2	9.634	1120500	7.75
3	10.582	6087785	42.10
4	12.605	6011661	41.58



	Retention Time	Area	% Area
1	7.022	629414	7.47
2	8.892	452449	5.37
3	9.780	5147386	61.05
4	11.855	2201915	26.12

Diethyl (*2S,5S*)-6-(2-fluoro-4-methylphenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3as):



96:4 dr, the major diastereomer was isolated as colorless oil in 67% yield, ee = 90%, $[\alpha]^{18}_D$ = +55.7 (*c* = 0.46, in CH_2Cl_2).

HPLC: Chiralcel IA, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 6.82 min, t_{r2} = 13.49 min.

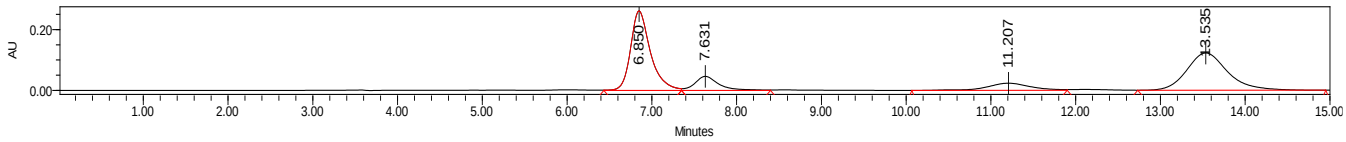
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, J = 7.8 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.0 Hz, 1H), 6.93 – 6.83 (m, 3H), 6.56 (s, 1H), 6.52 (s, 1H), 6.45 (s, 1H), 5.88 (s, 2H), 5.22 (s, 1H), 4.19 – 4.06 (m, 4H), 3.78 (s, 3H), 2.37 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.5, 166.9, 159.1 (d, J = 247.3 Hz), 158.9, 151.2, 146.6, 144.7, 141.6 (d, J = 8.1 Hz), 131.5, 130.7 , 128.2 (d, J = 3.3 Hz), 124.6 (d, J = 2.9 Hz), 123.8, 122.5 (d, J = 11.8 Hz), 115.7 (d, J = 20.6 Hz), 114,0, 109.9, 102.0, 101.5, 99.2, 85.2, 62.2, 62.1, 55.2, 52.4, 21.3, 13.9, 13.7.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –120.2 (s, 1F).

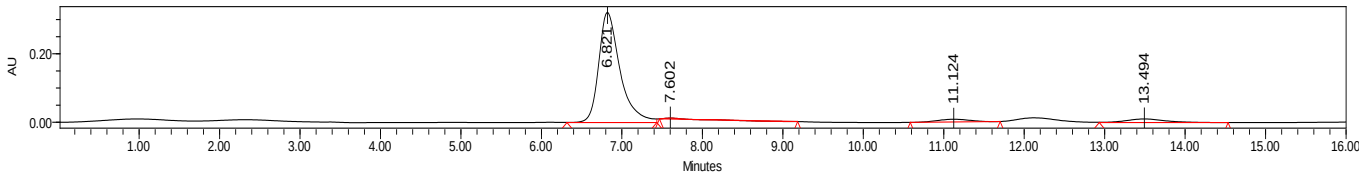
HRMS (ESI) Calculated for $C_{30}H_{29}FO_9$ ([M]+Na$^+$) = 575.1687, Found 575.1689.

IR (neat): 2981, 2904, 1745, 1631, 1510, 1480, 1239, 1171, 1037, 989, 938, 863, 838, 818, 733, 587 cm^{-1}.



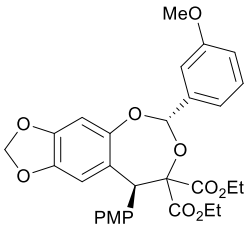
	Retention Time	Area	% Area
1	6.850	4252372	41.99
2	7.631	918636	9.07
3	11.207	846423	8.36

4	13.535	4108852	40.58



	Retention Time	Area	% Area
1	6.821	5927401	90.18
2	7.602	67099	1.02
3	11.124	222123	3.38
4	13.494	356366	5.42

Diethyl (*2S,5S*)-6-(3-methoxyphenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3at):



94:6 dr, the major diastereomer was isolated as white solid in 82% yield, m.p. = 58–63 °C, ee = 89%, $[\alpha]^{19}_D$ = +26.5 (*c* = 0.62, in CH_2Cl_2).

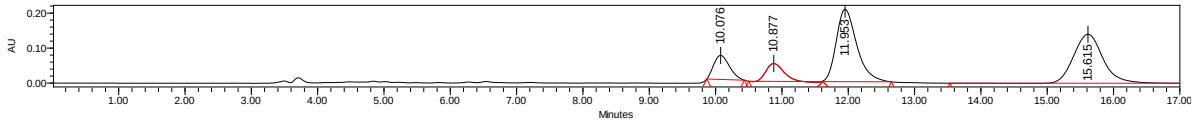
HPLC: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 11.86 min, t_{r2} = 15.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 9.9, 6.9 Hz, 3H), 7.32 – 7.27 (m, 2H), 6.95 – 6.90 (m, 1H), 6.90 – 6.84 (m, 2H), 6.54 (s, 1H), 6.47 (s, 1H), 6.18 (s, 1H), 5.88 (s, 2H), 5.20 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 4.08 – 4.00 (m, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H).

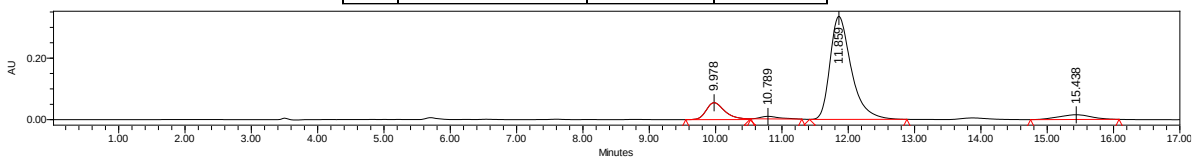
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.2, 167.0, 159.6, 158.9, 151.2, 146.6 , 144.6, 139.5, 131.7, 129.3, 124.2, 119.0, 114.7, 113.9, 112.2, 110.2, 103.4, 101.8, 101.6, 85.5, 62.1, 62.1, 55.3, 55.2, 52.9, 14.0, 13.6.

HRMS (ESI) Calculated for C30H30O10 ([M]+Na+) = 575.1731, Found 575.1725.

IR (neat): 2981, 2903, 1743, 1610, 1510, 1480, 1239, 1174, 1036, 994, 934, 863, 782, 735 cm^{-1}.

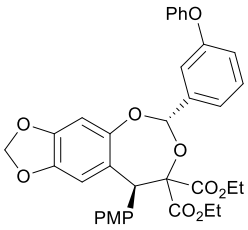


	Retention Time	Area	% Area
1	10.076	1130169	10.42
2	10.877	972893	8.97
3	11.953	4436445	40.90
4	15.615	4308703	39.72



	Retention Time	Area	% Area
1	9.978	1078956	11.69
2	10.789	167544	1.82
3	11.859	7455024	80.80
4	15.438	524745	5.69

Diethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(3-phenoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3au):



86:14 dr, the major diastereomer was isolated as colorless oil in 34% yield, m.p. = 56–61 °C, ee = 87%, $[\alpha]^{17}_D$ = +18.2 (*c* = 0.75, in CH_2Cl_2).

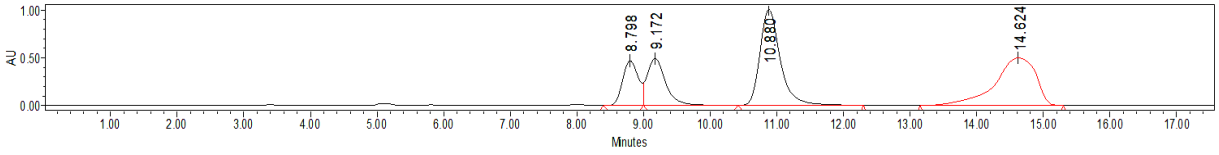
HPLC: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 10.94 min, t_{r2} = 13.93 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 2.0 Hz, 1H), 7.37 – 7.31 (m, 5H), 7.11 (d, J = 7.5 Hz, 1H), 7.05 (d, J = 1.1 Hz, 1H), 7.02 (d, J = 1.1 Hz, 2H), 6.85 (d, J = 9.1 Hz, 2H), 6.51 (s, 1H), 6.46 (s, 1H), 6.19 (s, 1H), 5.87 (s, 2H), 5.19 (s, 1H), 4.14 (q, J = 7.1 Hz, 2H), 4.03 (qd, J = 7.2, 2.6 Hz, 2H), 3.78 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H).

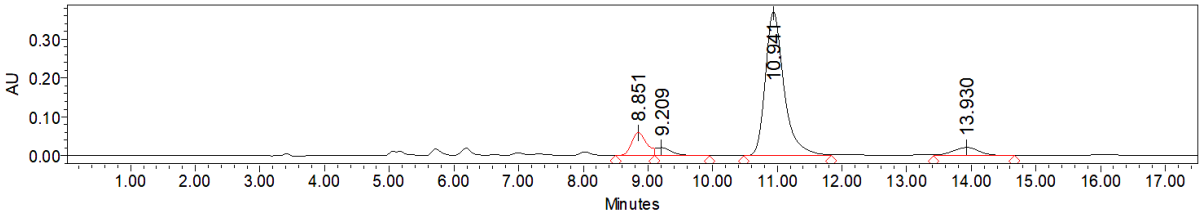
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.2, 166.9, 158.9, 157.2, 151.1, 146.6, 144.6, 140.0, 131.7, 130.4, 129.7, 129.6, 124.1, 123.3, 121.6, 119.4, 119.1, 118.9, 117.4, 113.9, 110.2, 103.1, 101.8, 101.6, 85.5, 62.2, 62.1, 55.2, 52.9, 14.0, 13.6.

HRMS (ESI) Calculated for C35H32O10 ([M]+Na+) = 635.1888, Found 635.1881.

IR (neat): 2981, 2904, 1744, 1610, 1585, 1510, 1246, 1174, 1036, 999, 936, 865, 837, 802, 735, 655 cm^{-1}.

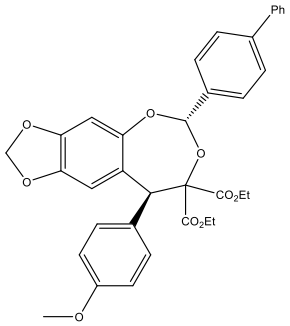


	Retention Time	Area	% Area
1	8.798	7761171	13.06
2	9.172	9432389	15.87
3	10.880	21177418	35.63
4	14.624	21064421	35.44



	Retention Time	Area	% Area
1	8.851	958602	10.29
2	9.209	355858	3.82
3	10.941	7408732	79.54
4	13.930	591167	6.35

Diethyl (*2S,5S*)-6-([1,1'-biphenyl]-4-yl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3av)



91:9 dr, the major diastereomer was isolated as yellow oil in 54% yield, 91% ee, $[\alpha]^{22}_D$ = -73.0 (*c* = 0.48, in CH_2Cl_2).

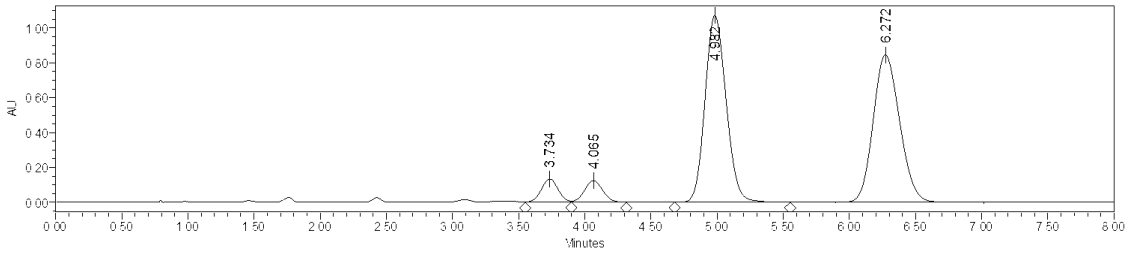
HPLC: UPC^2 Daicel CHIRALPAK IC-1, CO_2/^{i}PrOH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm, t_{r1} = 5.01 min, t_{r2} = 6.22 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.79 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.59 (m, 5H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.41 – 7.34 (m, 3H), 6.93 – 6.85 (m, 2H), 6.58 (s, 1H), 6.50 (s, 1H), 6.29 (s, 1H), 5.90 (s, 2H), 5.23 (s, 1H), 4.19 (qd, *J* = 7.1, 1.2 Hz, 2H), 4.11 – 4.02 (m, 2H), 3.80 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).

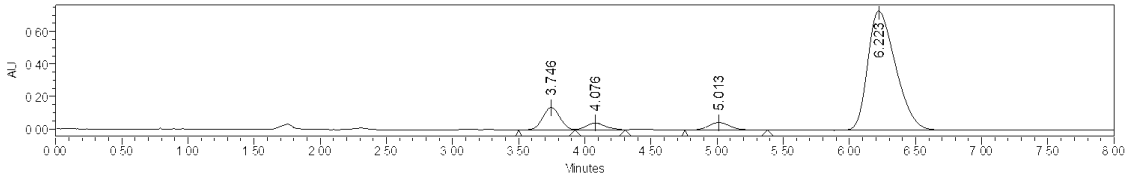
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ168.3 , 167.1 , 159.0 , 151.2 , 146.7 , 144.6 , 142.0 , 140.9, 137.1 , 131.7 , 130.5, 127.5 , 127.3 , 127.1 , 124.2 , 114.0 , 113.8, 110.3 , 103.5 , 101.9 , 101.6 , 85.5 , 62.2 , 62.1 , 55.3 , 52.9 , 14.0 , 13.6.

HRMS (ESI) Calculated for $C_{35}H_{32}O_9$ ([M+Na$^+$) = 619.1936, Found 619.1943.

IR (neat): 3386, 3028, 2954, 1747, 1602, 1504, 1434, 1228, 1066, 808, 755, 695 cm^{-1}.

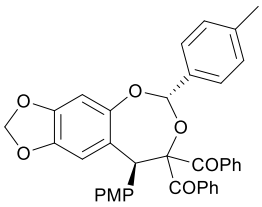


	Retention Time	Area	% Area
1	3.734	1171484	4.51
2	4.065	1181937	4.55
3	4.982	11862280	45.69
4	6.272	11744200	45.24



	Retention Time	Area	% Area
1	3.746	1241273	9.59
2	4.076	442858	3.42
3	5.013	527269	4.07
4	6.223	10732211	82.92

(*2S,5S*)-9-(4-methoxyphenyl)-6-(p-tolyl)-8,9-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8-diyl)bis(phenylmethanone) (3aw):



95:5 dr, the major diastereomer was isolated as white solid in 43% yield, m.p. = 149–153 °C, ee = 93%, $[\alpha]^{19}_D$ = –199.6 (*c* = 0.69, in CH_2Cl_2).

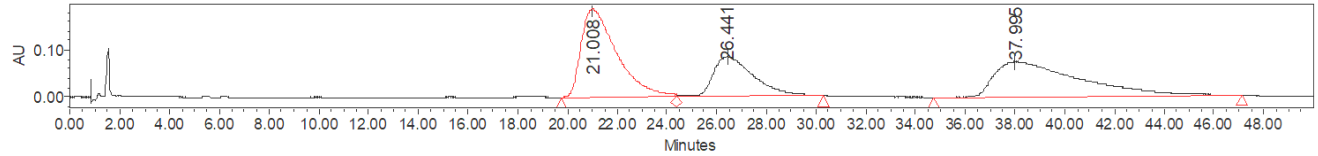
UPC^2 Daicel CHIRALPAK IC-1, CO_2/^{i}PrOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_{r1} = 22.47 min, t_{r2} = 44.79 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 9.6 Hz, 2H), 7.61 (d, J = 9.6 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 7.4 Hz, 2H), 7.20 (dd, J = 14.8, 7.6 Hz, 4H), 7.14 – 7.06 (m, 4H), 6.96 (s, 1H), 6.68 (d, J = 8.5 Hz, 2H), 6.57 (s, 1H), 5.95 (s, 1H), 5.90 (s, 1H), 5.65 (s, 1H), 5.21 (s, 1H), 3.66 (s, 3H), 2.32 (s, 3H).

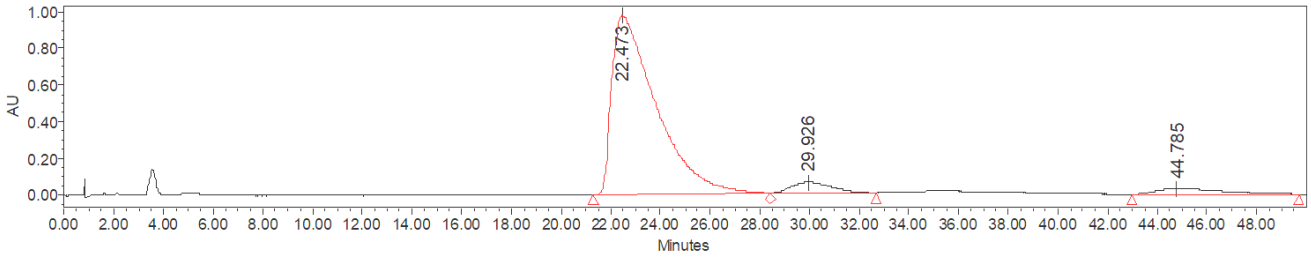
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.6, 194.3, 158.9, 150.8, 147.0, 144.7, 138.9, 135.7, 134.9, 133.7, 133.4, 132.5, 131.8, 130.6, 130.6, 129.9, 128.9, 128.4, 127.6, 126.4, 125.9, 114.0, 111.6, 102.9, 102.7, 101.7, 97.1, 58.0, 55.2, 21.2.

HRMS (ESI) Calculated for $C_{38}H_{30}O_7$ ([M+Na$^+$) = 621.1884, Found 621.1884.

IR (neat): 2923, 1697, 1667, 1610, 1510, 1481, 1234, 1180, 1162, 1035, 982, 895, 865, 812, 736, 637, 551 cm^{-1}.

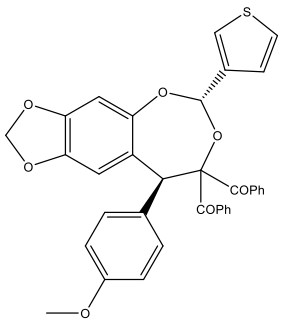


	Retention Time	Area	% Area
1	21.008	18676871	40.43
2	26.441	9659497	20.91
3	37.995	17854767	38.65



	Retention Time	Area	% Area
1	22.473	121368152	90.72
2	29.926	6749732	5.05
3	44.785	5660571	4.23

((*2S,5S*)-9-(4-methoxyphenyl)-6-(thiophen-3-yl)-8,9-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8-diyl)bis(phenylmethanone) (3ax)



85:15 dr, the major diastereomer was isolated as yellow oil in 51% yield, 80% ee, $[\alpha]^{23}_{D}$ = -147.6 (*c* = 0.58, in CH_2Cl_2).

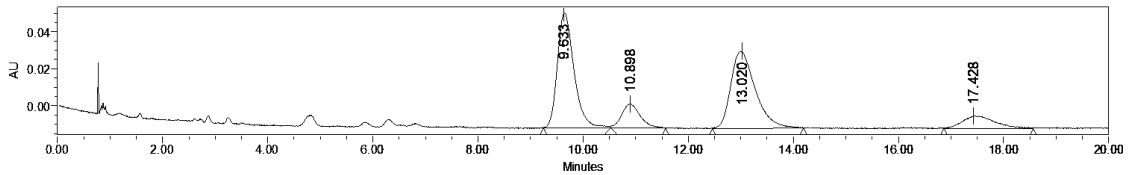
HPLC: UPC^2 Daicel CHIRALPAK IA-1, CO_2/^{i}PrOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm, t_{r1} = 9.25 min, t_{r2} = 12.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 2H), 7.64 – 7.60 (m, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.25 – 7.18 (m, 6H), 7.13 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.01 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.95 (s, 1H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.59 (s, 1H), 5.96 (d, *J* = 1.5 Hz, 1H), 5.91 (d, *J* = 1.5 Hz, 1H), 5.72 (s, 1H), 5.20 (s, 1H), 3.64 (s, 3H).

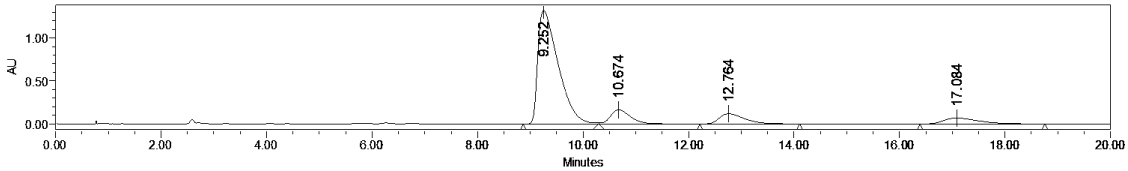
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.4, 194.2 , 158.9 , 150.5 , 147.1, 144.8 , 139.3 , 135.6, 133.7 , 133.6 , 132.7 , 131.8 , 130.6 , 129.8 , 128.4 , 127.7 , 126.4 , 126.0 , 125.8 , 123.4 , 114.0 , 111.6 , 102.8 , 101.7 , 99.6 , 97.1 , 58.0 , 55.2.

HRMS (ESI) Calculated for $C_{35}H_{26}O_7S$ ([M]+Na$^+$) = 613.1291, Found 613.1291.

IR (neat): 3063, 2899, 2836, 1698, 1508, 1481, 1239, 1180, 1034, 1001, 789, 695 cm^{-1}.



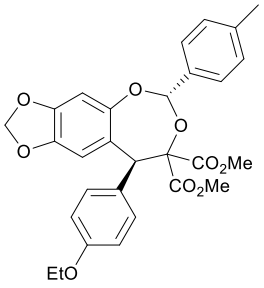
	Retention Time	Area	% Area
1	9.633	1365073	41.15
2	10.898	313556	9.45
3	13.020	1352225	40.76
4	17.428	286639	8.64



	Retention Time	Area	% Area
1	9.252	35481046	75.31
2	10.674	4419197	9.38

3	12.764	4010202	8.51
4	17.084	3200171	6.79

Dimethyl (*2S,5S*)-9-(4-ethoxyphenyl)-6-(p-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ba):



92:8 dr, the major diastereomer was isolated as white solid in 84% yield, m.p. = 67–74 °C, ee = 95%, $[\alpha]^{18}_D$ = +36.3 (*c* = 0.76, in CH_2Cl_2).

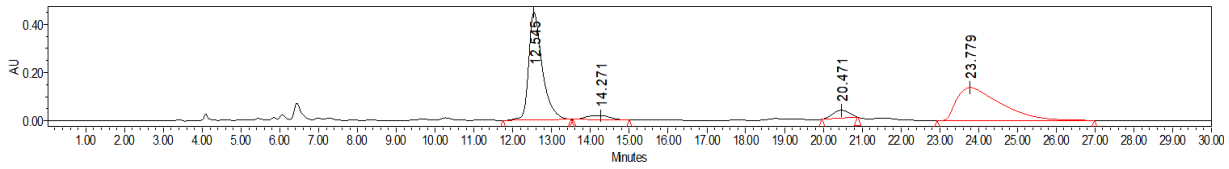
HPLC: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 12.94 min, t_{r2} = 25.63 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 6.88 – 6.82 (m, 2H), 6.53 (s, 1H), 6.48 (s, 1H), 6.25 (s, 1H), 5.89 (s, 2H), 5.21 (s, 1H), 4.01 (q, J = 7.0 Hz, 2H), 3.68 (s, 3H), 3.60 (s, 3H), 2.38 (s, 3H), 1.41 (t, J = 7.0 Hz, 3H).

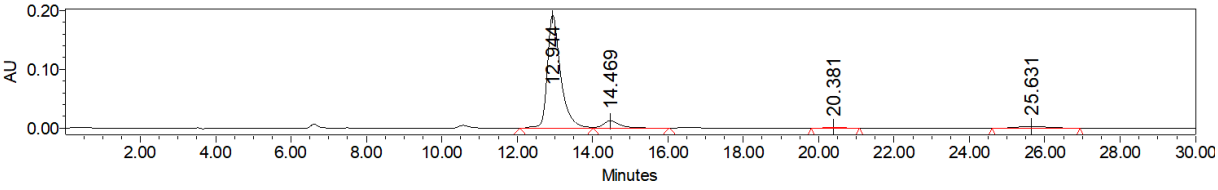
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 167.7, 158.3, 151.3, 146.7, 144.6, 139.0, 135.1, 131.5, 129.0, 126.4, 123.7, 114.5, 110.2, 103.9, 101.9, 101.6, 85.6, 63.4, 53.0, 52.9, 52.9, 21.3, 14.9.

HRMS (ESI) Calculated for $C_{29}H_{28}O_9$ ([M]+Na^+) = 543.1626, Found 543.1623.

IR (neat): 2980, 2952, 2899, 1747, 1610, 1509, 1480, 1238, 1171, 1038, 936, 882, 867, 841, 812, 735 cm^{-1}.

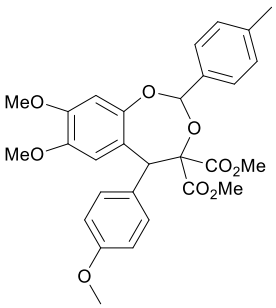


	Retention Time	Area	% Area
1	12.545	10840748	46.69
2	14.271	691319	2.98
3	20.471	952431	4.10
4	23.779	10735711	46.23



	Retention Time	Area	% Area
1	12.944	4719617	89.28
2	14.469	381252	7.21
3	20.381	28300	0.54
4	25.631	157334	2.98

Dimethyl 7,8-dimethoxy-5-(4-methoxyphenyl)-2-(p-tolyl)benzo[d][1,3]dioxepine-4,4(5H)-dicarboxylate (6a):



the major diastereomer was isolated as colorless oil in 43% yield, ee = 43%, $[\alpha]^{25}_D$ = +32.0 (*c* = 0.30, in CH_2Cl_2).

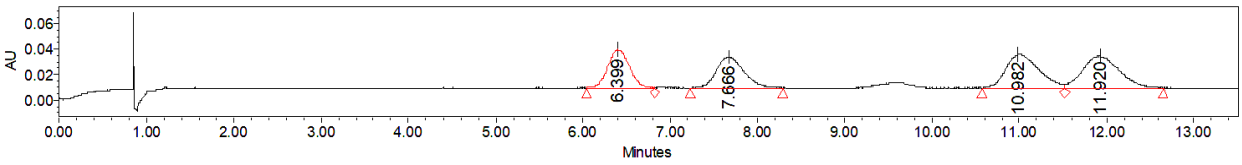
UPC^2 Daicel CHIRALPAK IC-3, CO_2/CH_3CH_2OH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_{r1} = 10.77 min, t_{r2} = 11.60 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.54 (s, 1H), 6.49 (s, 1H), 6.39 (s, 1H), 5.26 (s, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.70 (s, 3H), 3.68 (s, 3H), 3.65 (s, 3H), 2.38 (s, 3H).

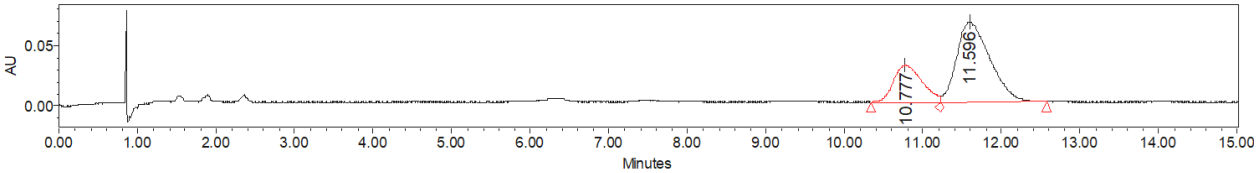
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.4, 167.7, 158.9, 150.3, 148.2, 145.9, 139.0, 135.2, 131.2, 130.9, 129.0, 126.5, 121.5, 114.0, 113.6, 104.0, 85.6, 56.2, 55.9, 55.2, 53.0, 52.9, 52.4, 21.3.

HRMS (ESI) Calculated for $C_{29}H_{30}O_9$ ([M]+Na$^+$) = 545.1782, Found 545.1773.

IR (neat): 2953, 1750, 1611, 1510, 1442, 1365, 1305, 1242, 1219, 1123, 1021, 940, 810, 736 cm^{-1}.



	Retention Time	Area	% Area
1	6.399	508055	20.87
2	7.666	531604	21.84
3	10.982	679519	27.91
4	11.920	715112	29.38



	Retention Time	Area	% Area
1	10.777	776713	28.41
2	11.596	1957035	71.59

the minor diastereomer was isolated as colorless oil in 41% yield, ee = 76%, $[\alpha]^{26}_D$ = -36.2 (*c* = 0.17, in CH_2Cl_2).

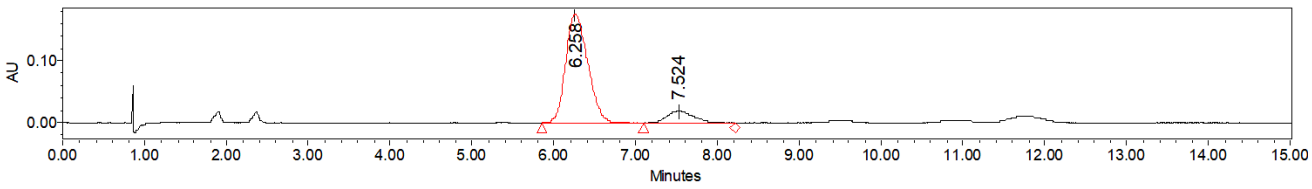
UPC^2 Daicel CHIRALPAK IC-3, CO_2/CH_3CH_2OH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm, t_{r1} = 6.26 min, t_{r2} = 7.52 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.9 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.27 (s, 2H), 6.82 (s, 1H), 6.76 (d, J = 8.8 Hz, 2H), 6.63 (s, 1H), 5.77 (s, 1H), 4.93 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.57 (s, 3H), 2.40 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.1, 167.0, 158.8, 150.3, 148.6, 145.8, 138.9, 135.2, 131.1, 130.5, 129.0, 126.3, 123.2, 114.3, 113.8, 105.4, 102.2, 86.8, 56.6, 56.2, 56.0, 55.1, 53.3, 53.1, 21.3.

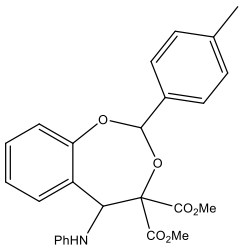
HRMS (ESI) Calculated for $C_{29}H_{30}O_9$ ([M]+Na$^+$) = 545.1782, Found 545.1774.

IR (neat): 2953, 1750, 1612, 1511, 1442, 1347, 1306, 1233, 1199, 1033, 812, 795 cm^{-1}.



	Retention Time	Area	% Area
1	6.258	3299908	88.00
2	7.524	450058	12.00

Dimethyl 5-(phenylamino)-2-(p-tolyl)benzo[d][1,3]dioxepine-4,4(5H)-dicarboxylate (3da)



94:6 dr, the major diastereomer was isolated as yellow oil in 43% yield, 51% ee, $[\alpha]^{20}_D$ = -103.0 (*c* = 0.86, in CH_2Cl_2).

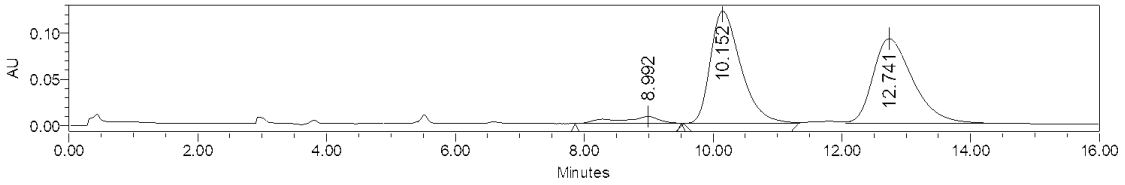
HPLC: Chiralcel ODH, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 11.20 min, t_{r2} = 14.40 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.73 – 7.67 (m, 2H), 7.41 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.16 (m, 1H), 7.08 (dddd, *J* = 14.7, 13.5, 7.3, 1.6 Hz, 4H), 6.74 – 6.67 (m, 3H), 5.86 (s, 1H), 5.58 (s, 1H), 4.91 (s, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 2.42 (s, 3H).

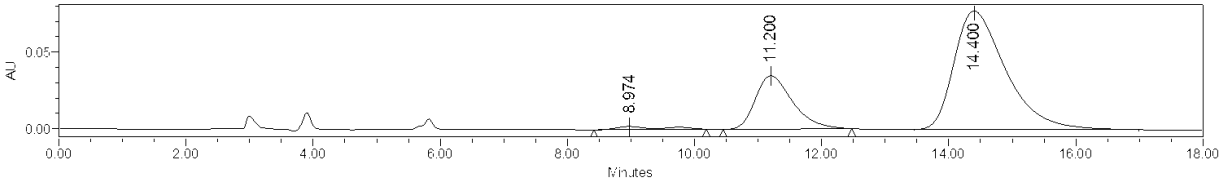
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ166.5 , 157.4 , 145.9 , 139.0 , 134.7 , 132.1 , 130.2 , 129.5 , 129.1 , 126.3 , 124.6 , 121.4 , 118.9 , 115.2 , 102.3 , 85.9 , 62.8 , 53.8 , 53.3 , 21.3

HRMS (ESI) Calculated for $C_{26}H_{25}O_6N$ ([M]+H^+) =571.1938, Found 571.1937.

IR (neat): 3384, 3026, 2954, 1745, 1602, 1504, 1434, 1227, 1066, 881, 808, 755, 695 cm^{-1}.

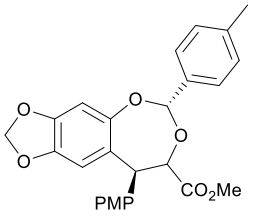


	Retention Time	Area	% Area
1	8.992	331645	4.04
2	10.152	3978446	48.48
3	12.741	3895780	47.48



	Retention Time	Area	% Area
1	8.974	98511	1.67
2	11.200	1419686	24.08
3	14.400	4377080	74.25

Methyl (2*S*, 6*S*)-9-(4-methoxyphenyl)-6-(p-tolyl)-8,9-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8-carboxylate (4a):



65:35 dr, the major diastereomer was isolated as white solid in 78% yield, m.p. = 59–63 °C, ee = 99/96%.

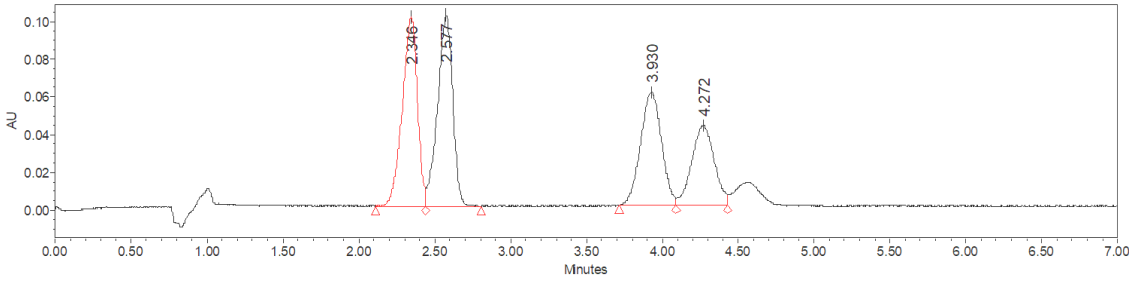
UPC^2 Daicel CHIRALPAK IC-3, CO_2/CH_3OH = 80/20, flow rate = 1.5 mL/min, λ = 225 nm, t_{r1} = 2.37 min, t_{r2} = 2.59 min.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39, 7.23 (d, J = 7.9 Hz, 2H), 7.15 – 7.08 (m, 4H), 6.78 (dd, J = 8.5, 6.5 Hz, 2H), 6.28, 6.24 (s, 1H), 6.18, 6.14 (s, 1H), 6.58, 5.92 (s, 1H), 5.82 (d, J = 5.4 Hz, 1H), 5.75 (d, J = 8.6 Hz, 1H), 5.33, 4.77 (d, J = 3.2 Hz, J = 9.8 Hz, 1H), 4.63, 4.51 (d, J = 3.2 Hz, J = 9.8 Hz, 1H), 3.70 (s, 3H), 3.51, 3.50 (s, 3H), 2.28, 2.27 (s, 3H).

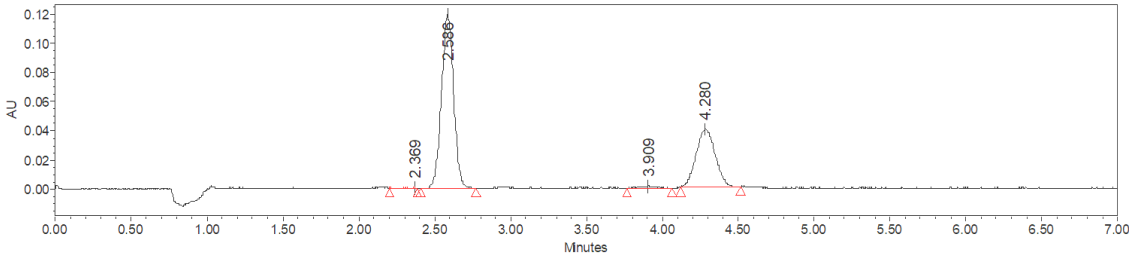
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 170.3, 158.9, 146.6, 146.4, 144.6, 139.1, 134.2, 132.4, 130.0, 128.7, 127.3, 126.4, 114.1, 109.5, 104.2, 103.8, 101.7, 80.0, 55.2, 52.4, 51.4, 21.0.

HRMS (ESI) Calculated for $C_{26}H_{24}O_7$ ([M+Na$^+$) = 471.1414, Found 471.1404.

IR (neat): 2952, 2901, 1747, 1611, 1509, 1480, 1237, 1205, 1171, 1151, 1094, 1032, 935, 837, 813, 710 cm^{-1}.

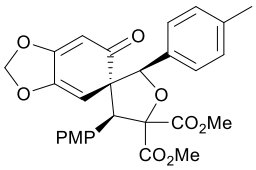


	Retention Time	Area	% Area
1	2.346	695327	28.81
2	2.577	706282	29.27
3	3.930	573679	23.77
4	4.272	438013	18.15



	Retention Time	Area	% Area
1	2.369	1543	0.15
2	2.586	661392	65.12
3	3.909	5492	0.54
4	4.280	347287	34.19

Dimethyl (1*R*,4*S*,5*S*)-4'-(4-methoxyphenyl)-6-oxo-2'-(p-tolyl)-2'H,6H-spiro[benzo[d][1,3]dioxole-5,3'-furan]-5',5'(4'H)-dicarboxylate (5a):



19:1 d.r., the major diastereomer was isolated as white solid in 48% yield, m.p. = 73 – 78 °C, 96% ee, $[\alpha]^{23}_D$ = -41.0 (*c* = 0.96, in CH_2Cl_2).

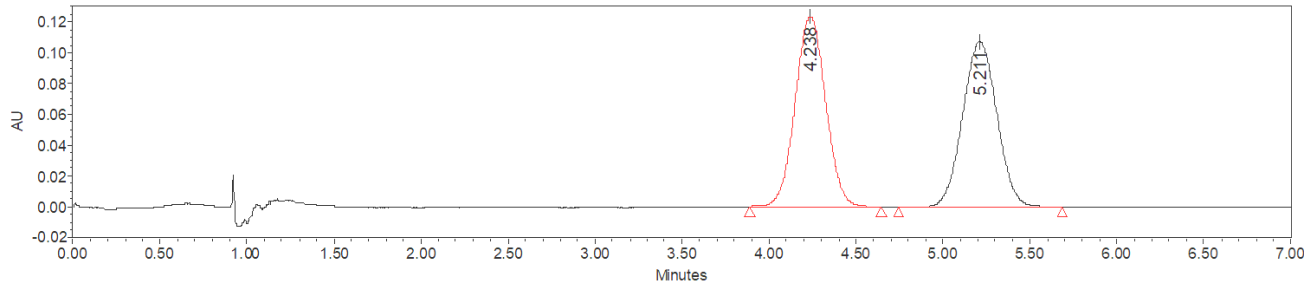
HPLC: CHIRALPAK IC-3, CO2/EtOH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm, t_{r1} = 4.24 min, t_{r2} = 5.21 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.11 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.37 (s, 1H), 5.55 (s, 1H), 5.52 (s, 1H), 5.47 (d, *J* = 1.2 Hz, 2H), 5.16 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.53 (s, 3H), 2.30 (s, 3H).

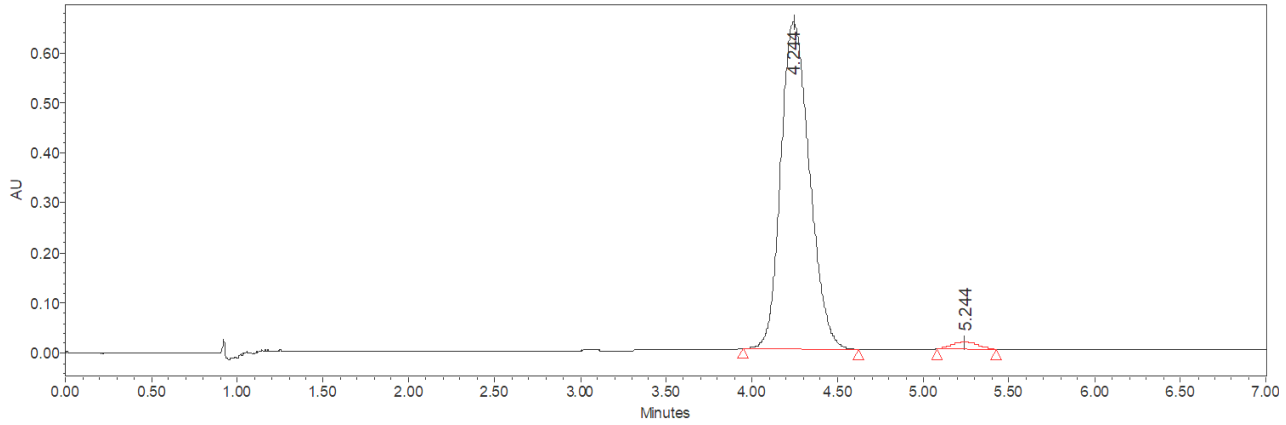
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.3 , 169.4, 169.2 , 163.8 , 159.3 , 144.3 , 137.7 , 132.6, 131.2 , 128.7 , 125.8 , 125.0 , 113.3 , 104.4 , 101.3 , 99.8 , 90.5 , 87.5 , 66.1 , 64.20 , 55.1 , 53.4 , 52.7 , 21.3 .

HRMS (ESI) Calculated for $C_{28}H_{26}O_9$ ([M+Na$^+$) = 529.1469, Found 529.1477.

IR (neat): 2954, 1740, 1630, 1745, 1514, 1434, 1513, 1281, 1183, 1152, 1079, 1035, 943, 845, 823, 755, 735, 569 cm^{-1}.

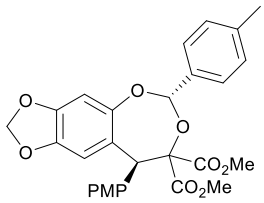


	Retention Time	Area	% Area
1	4.238	1512324	50.57
2	5.211	1478508	49.43



	Retention Time	Area	% Area
1	4.244	7639872	97.94
2	5.244	161005	2.06

Dimethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(p-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3aa-after recrystallization):



After recrystallization: >19:1 dr, the major diastereomer was isolated as white solid in 93% yield, m.p. = 200–204 °C, 99% ee, $[\alpha]^{18}_{D}$ = +53.8 (*c* = 0.53, in CH_2Cl_2).

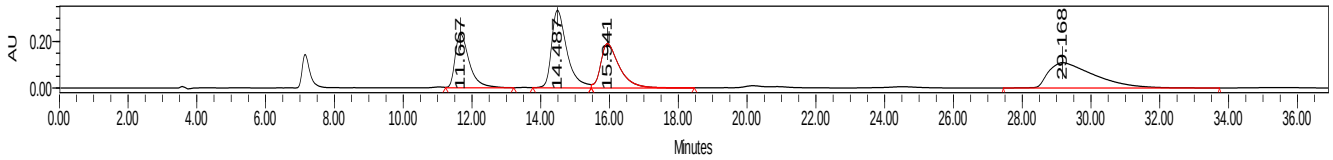
HPLC: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 15.11 min, t_{r2} = 30.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 6.54 (s, 1H), 6.48 (s, 1H), 6.26 (s, 1H), 5.89 (s, 2H), 5.22 (s, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.60 (s, 3H), 2.39 (s, 3H).

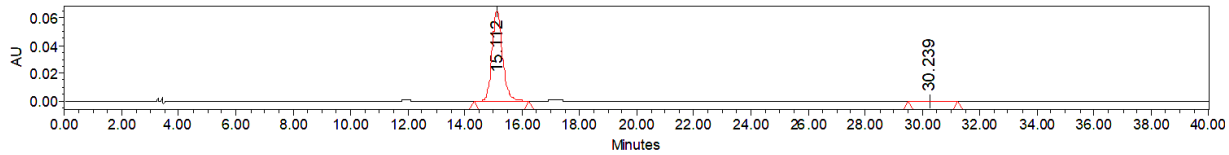
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 167.6, 158.9, 151.2, 146.7, 144.6, 139.0, 135.1, 131.5, 129.0, 126.4, 123.7, 114.0, 110.2, 103.9, 101.9, 101.6, 85.5, 55.2, 53.0, 52.9, 52.8, 21.3.

HRMS (ESI) Calculated for $C_{28}H_{26}O_9$ ([M]+Na^+) = 529.1469, Found 529.1459.

IR (neat): 3006, 2953, 2904, 1749, 1611, 1511, 1240, 1172, 1037, 1003, 937, 869, 838, 805 cm^{-1}.



	Retention Time	Area	% Area
1	11.667	6708252	19.57
2	14.487	10364261	30.24
3	15.941	7152558	20.87
4	29.168	10051679	29.33



	Retention Time	Area	% Area
1	15.112	1679534	99.86
2	30.239	2417	0.14

13 References

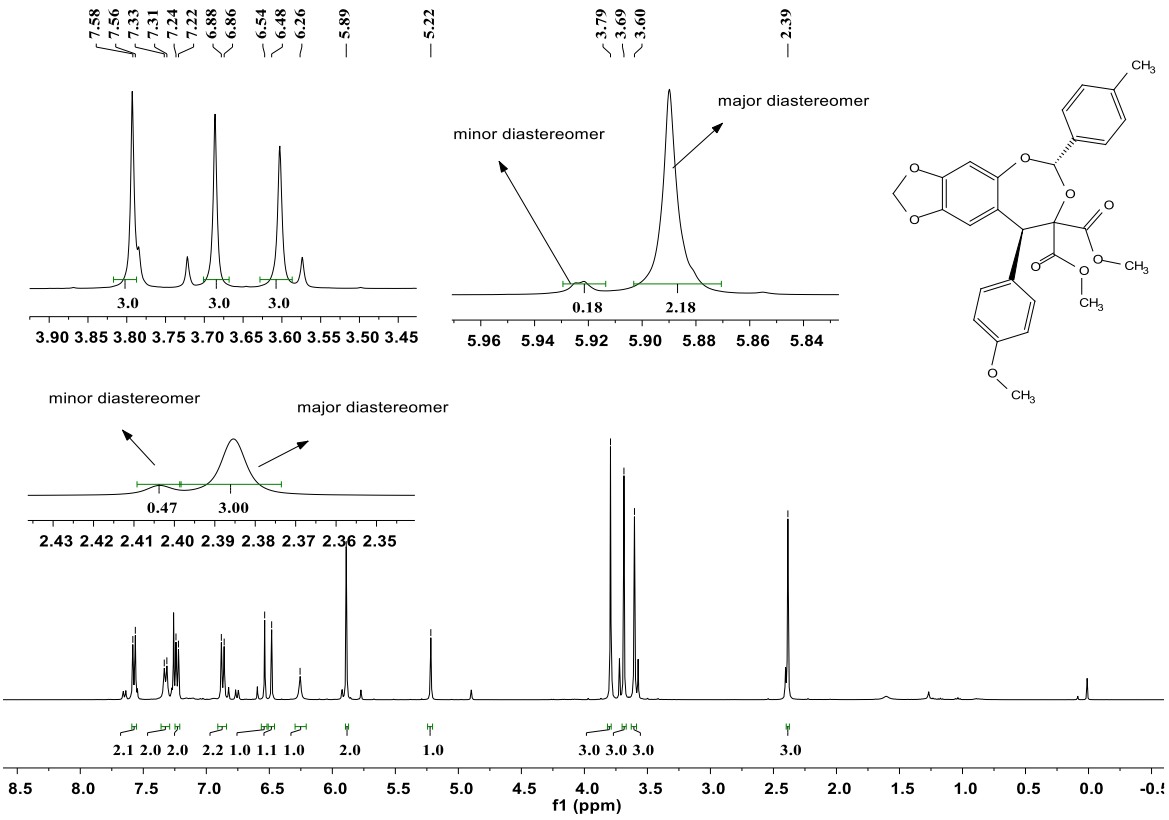
1 (a) Wen, Y. H.; Huang, X.; Huang, J. L.; Xiong, Y.; Qin, B.; Feng, X. M. Asymmetric Cyanosilylation of Aldehydes Catalyzed by Novel Organo-catalysts.*Synlett*., 2005, **16**, 2445. (b) Liu, X. H.; Feng, X. M. Chiral *N,N'*-Dioxides: New Ligands and Organocatalysts for Catalytic Asymmetric Reactions. *Acc. Chem. Res*.**,** 2011, **44**, 574.

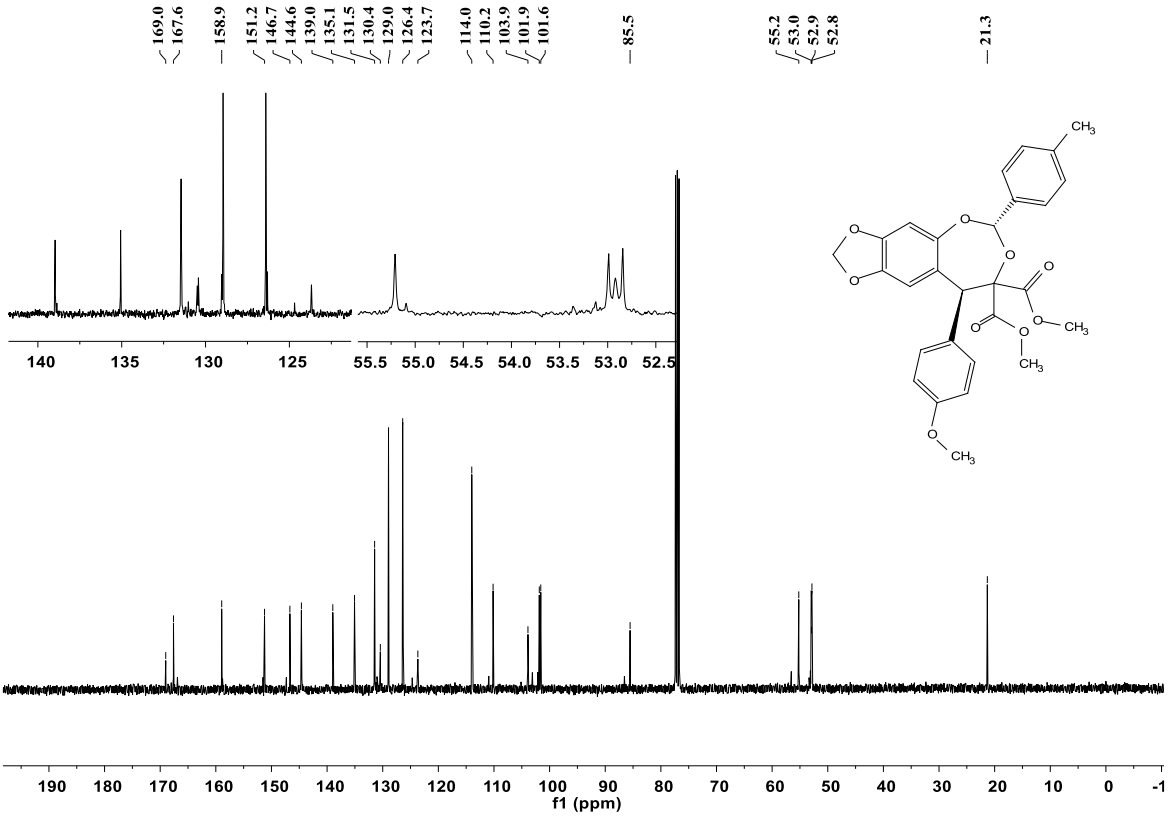
2 Yuan, X.; Lin, L. L.; Chen, W. L.; Wu, W. B.; Liu, X. H.; Feng, X. M. Synthesis of Chiral Tetrahydrofurans via Catalytic Asymmetric [3 + 2] Cycloaddition of Heterosubstituted Alkenes with Oxiranes. *J. Org. Chem*., 2016, **81**, 1237−1243.

3 Zhang, S. S.; Wang, D. C.; Xie, M. S.; Qu, G. R.; Guo, H. M.; Highly Chemo- and Diatereoselective Dearomative [3+2] Cycloaddition Reactions of Benzazoles with Donor–Acceptor Oxiranes. *Org. Lett*.**,** 2018, **20**, 8026.

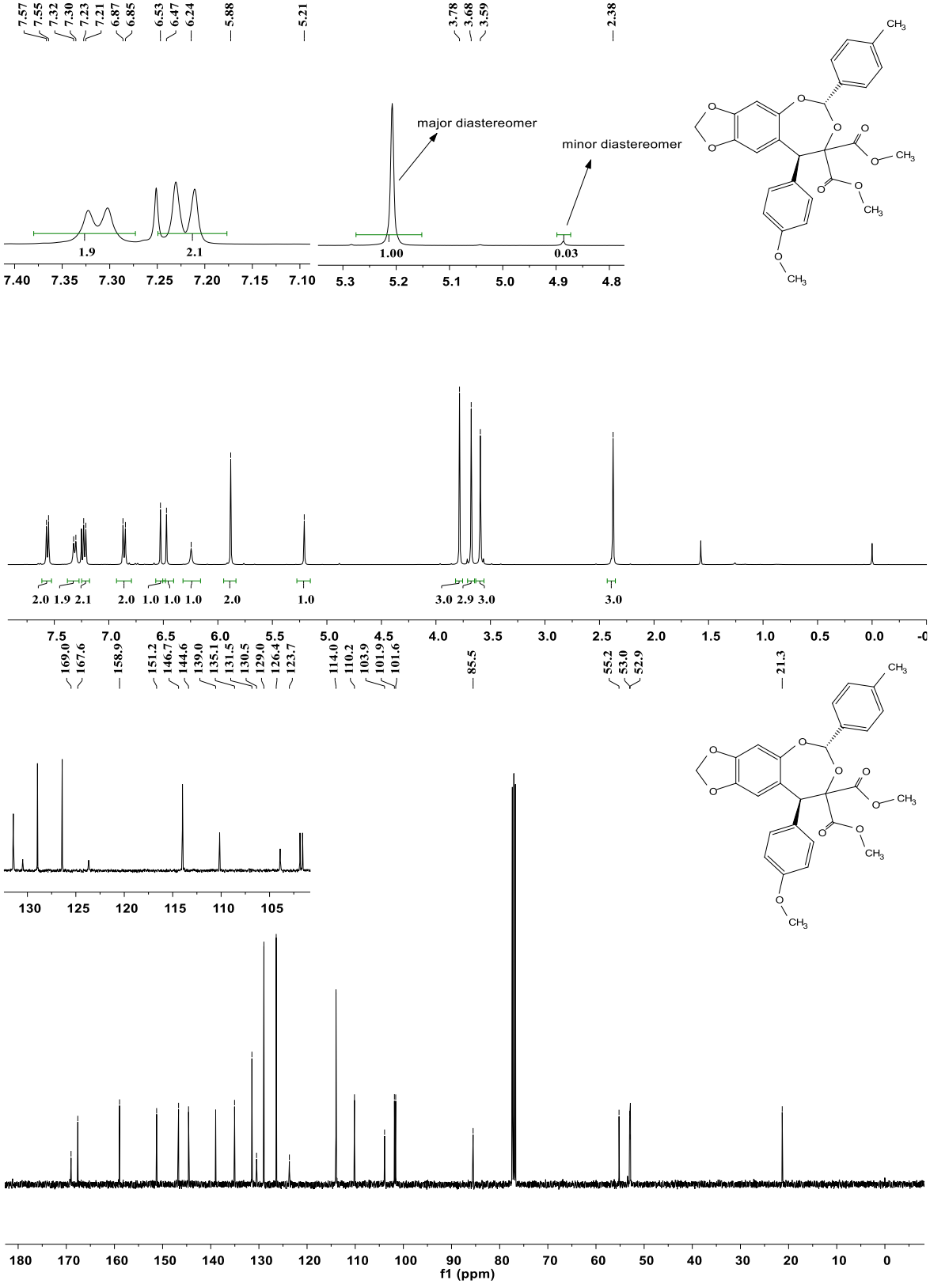
14 Copies of NMR Spectra for Products

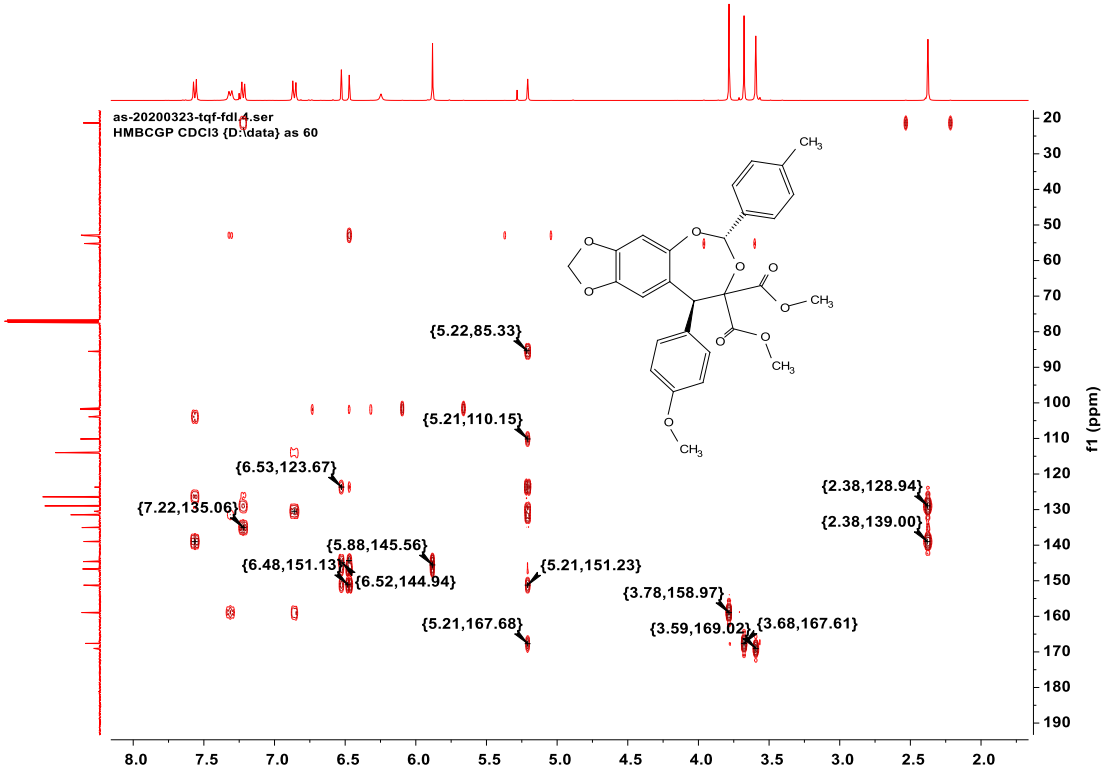
Dimethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(p-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3aa):

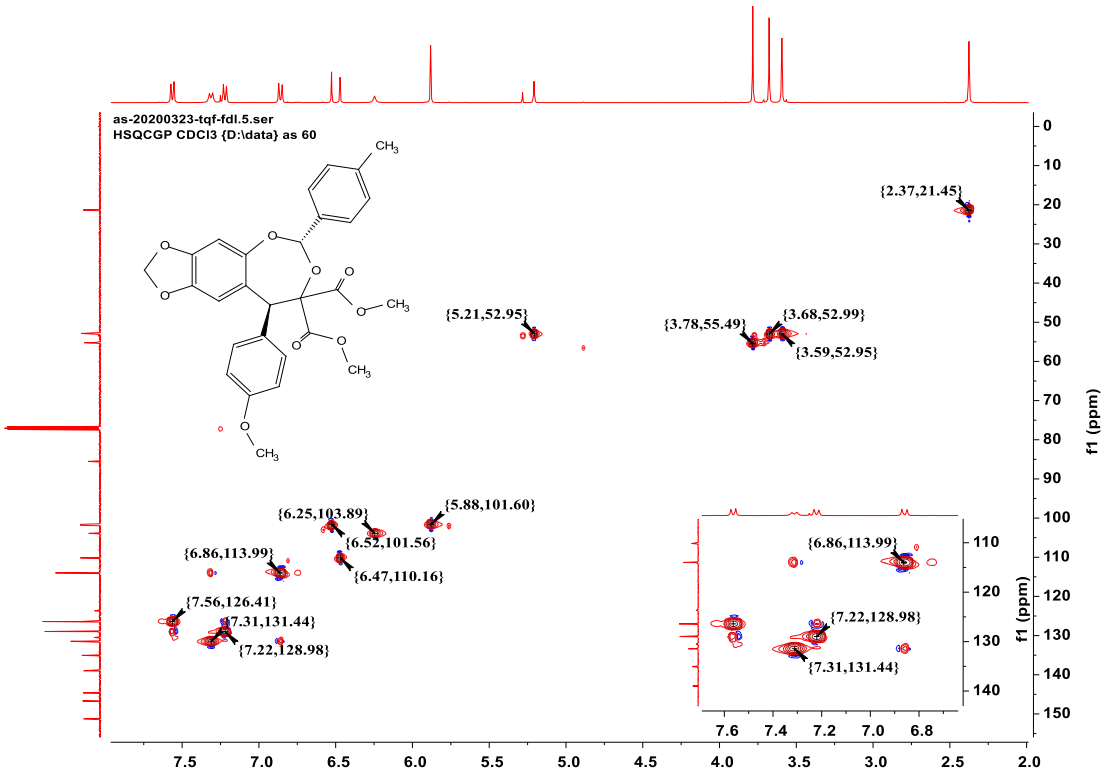


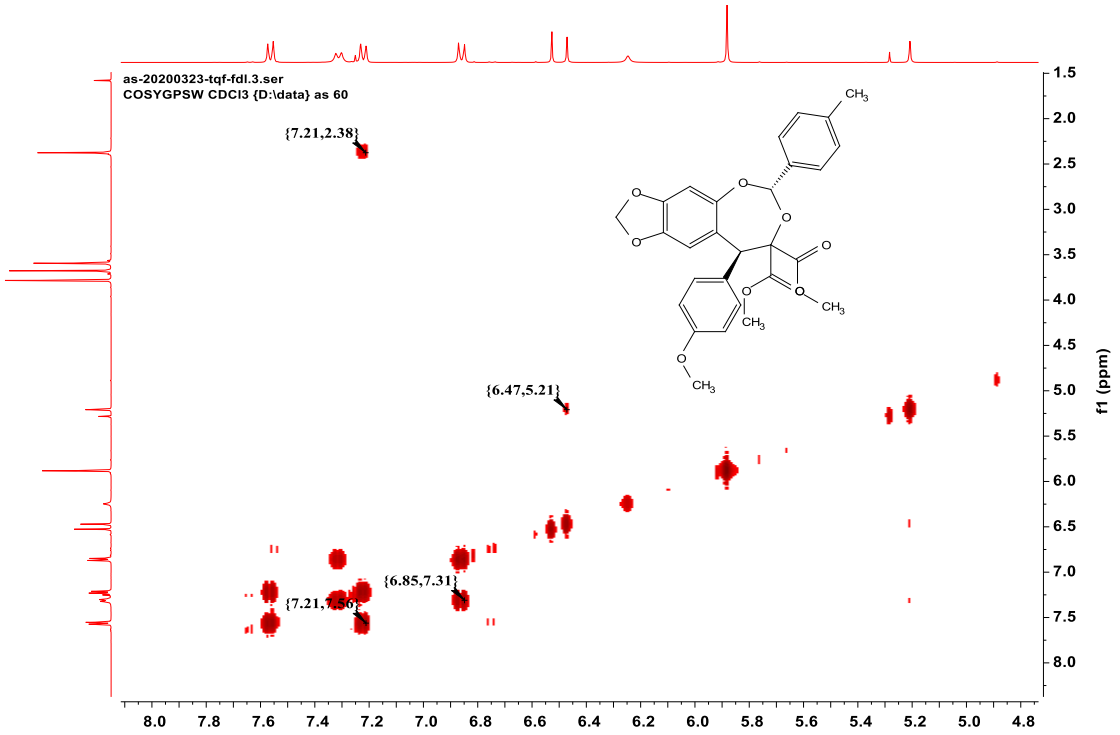


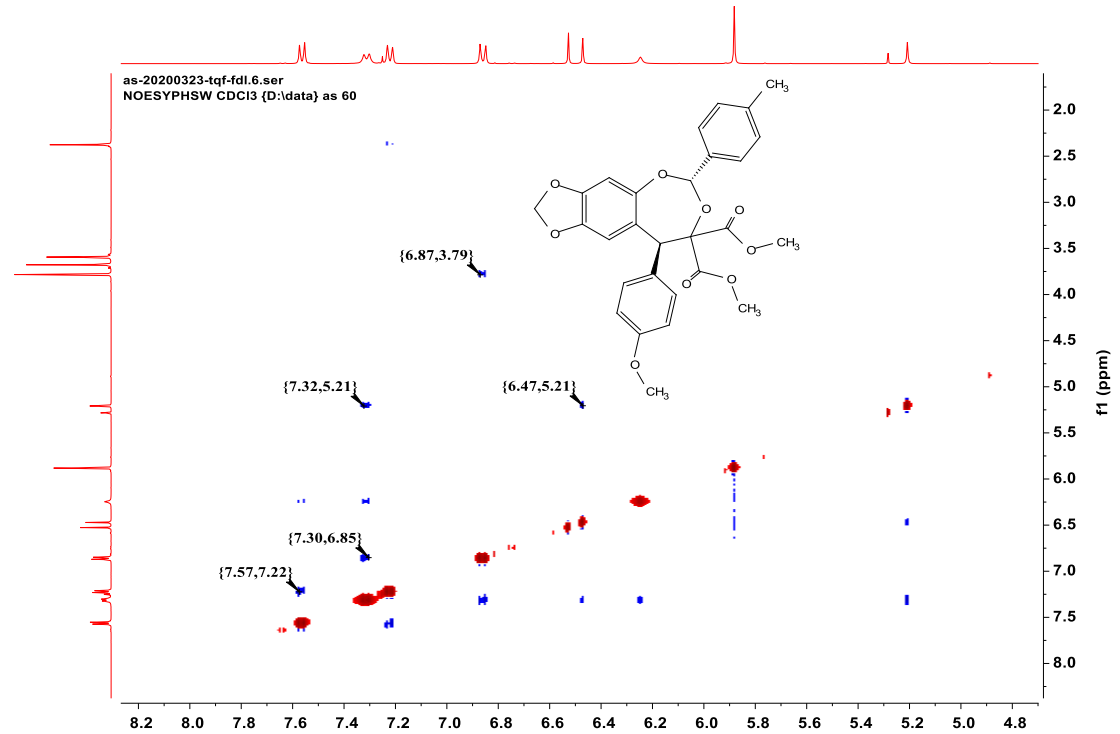
Dimethyl (*2S,5S*)-9-(4-ethylphenyl)-6-(p-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3aa-after recrystallization):



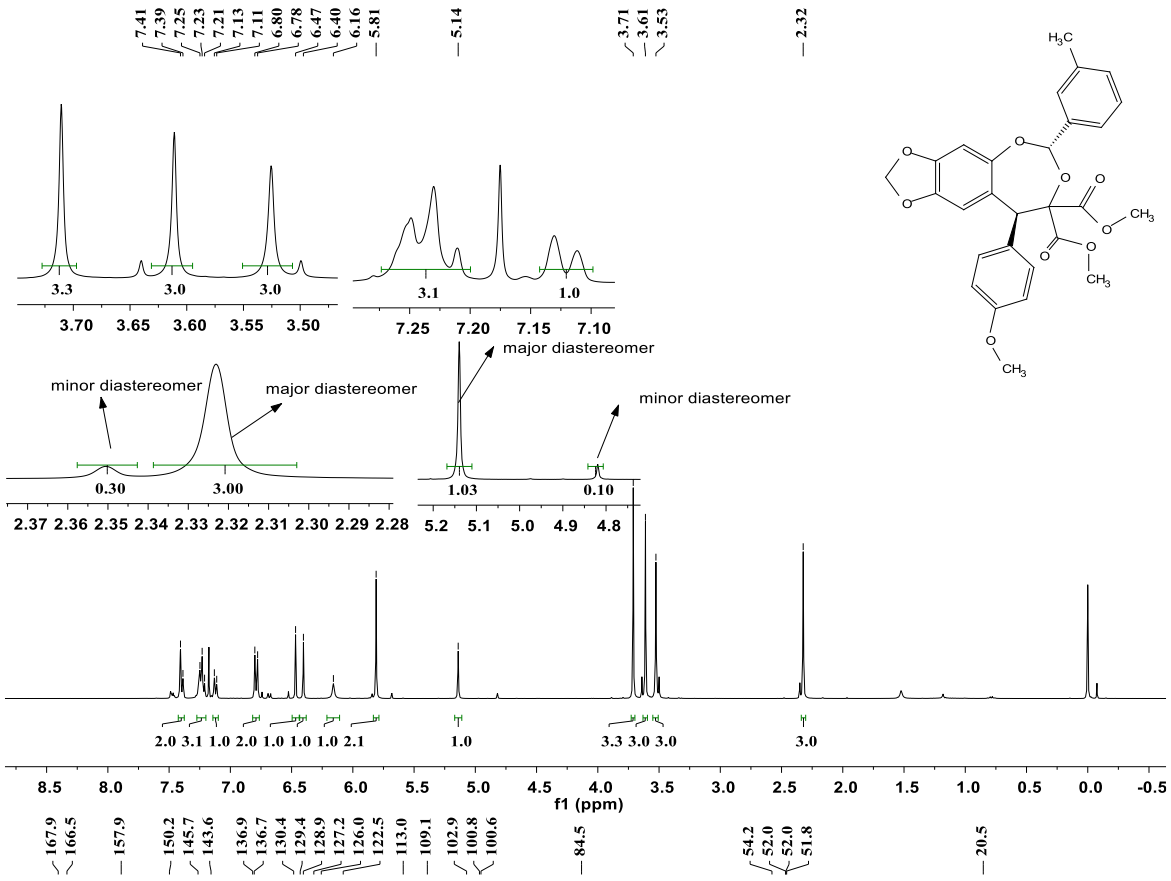

as-20200323-tqf-fdl.4.ser
HMBCGP CDCl3 {D:\data} as 60
{5.22,85.33}
{5.21,110.15}
{6.53,123.67}
{7.22,135.06}
{5.88,145.56}
{6.48,151.13}
{6.52,144.94}
{5.21,151.23}
{3.78,158.97}
{5.21,167.68}
{3.59,169.02}
{3.68,167.61}
{2.38,128.94}
{2.38,139.00}
f1 (ppm)

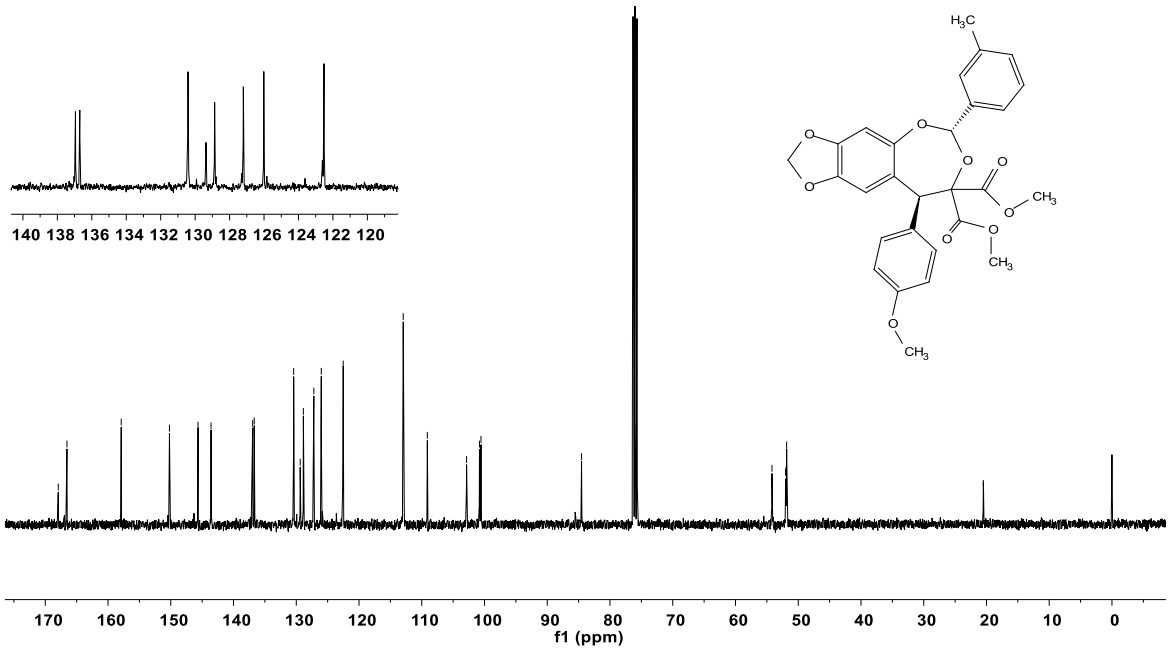

as-20200323-tqf-fdl.5.ser
HSQCGP CDCl3 {D:\data} as 60
{2.37,21.45}
{5.21,52.95}
{3.78,55.49}
{3.68,52.99}
{3.59,52.95}
{6.25,103.89}
{5.88,101.60}
{6.52,101.56}
{6.86,113.99}
{6.47,110.16}
{7.56,126.41}
{7.31,131.44}
{7.22,128.98}
{6.86,113.99}
{7.22,128.98}
{7.31,131.44}
f1 (ppm)


as-20200323-tqf-fdl.3.ser
COSYGPSW CDCl3 {D:\data} as 60
{7.21,2.38}
{6.47,5.21}
{6.85,7.31}
{7.21,7.56}
f1 (ppm)

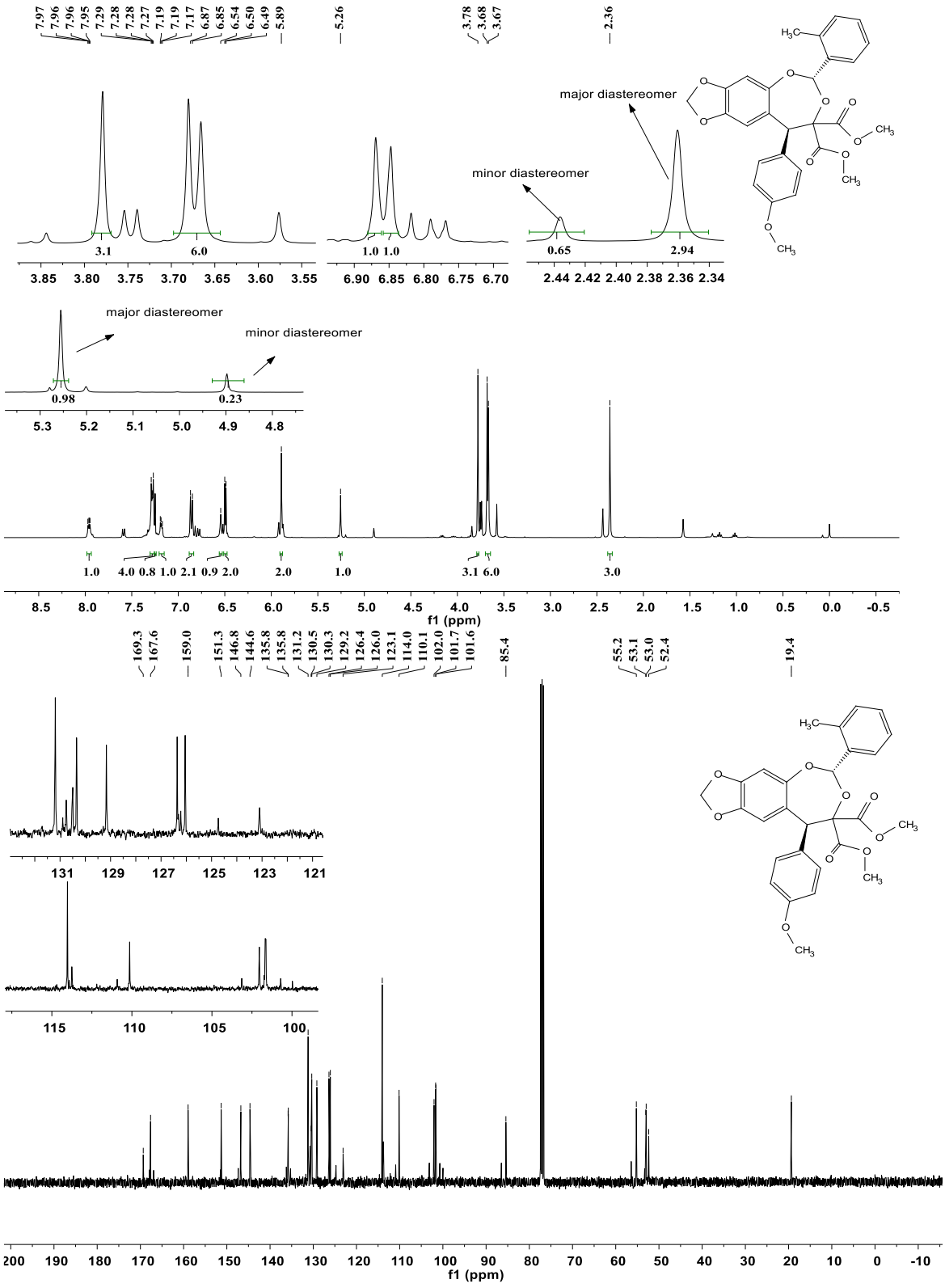

as-20200323-tqf-fdl.6.ser
NOESYPHSW CDCl3 {D:\data} as 60
{6.87,3.79}
{7.32,5.21}
{6.47,5.21}
{7.30,6.85}
{7.57,7.22}
f1 (ppm)

Dimethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(m-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ab):

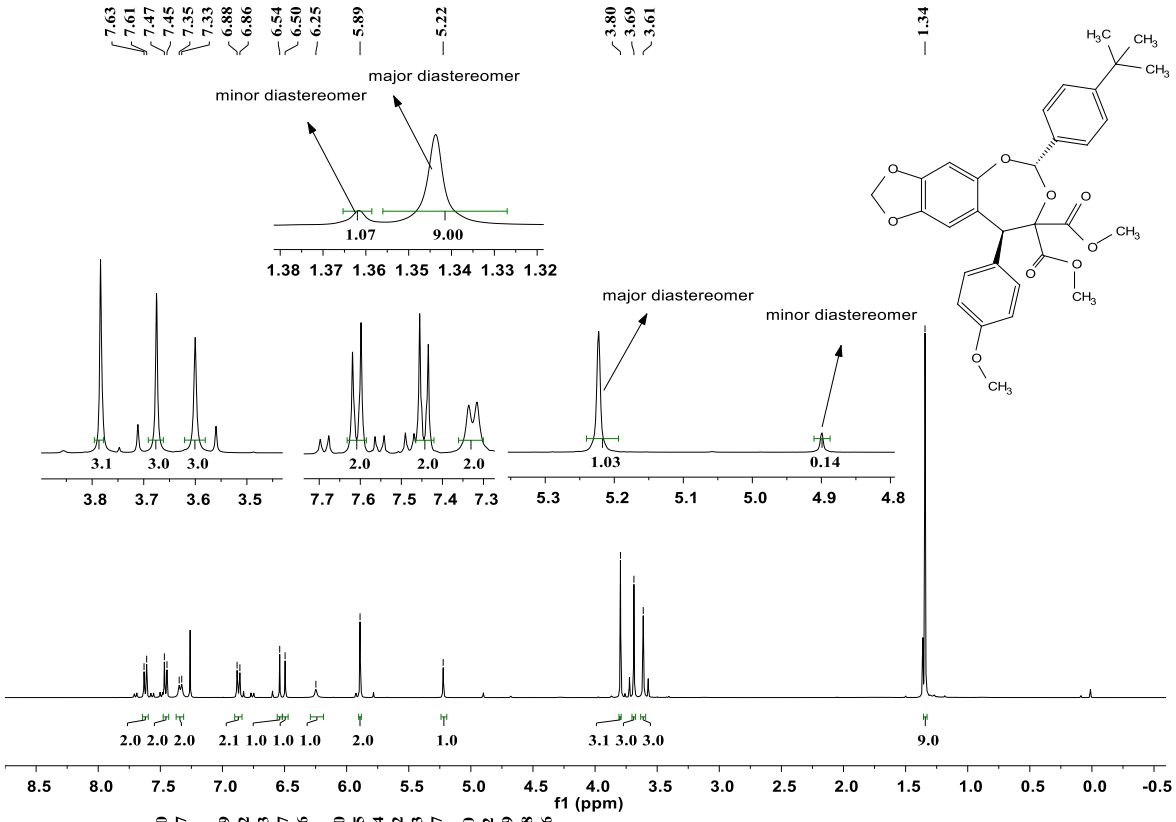


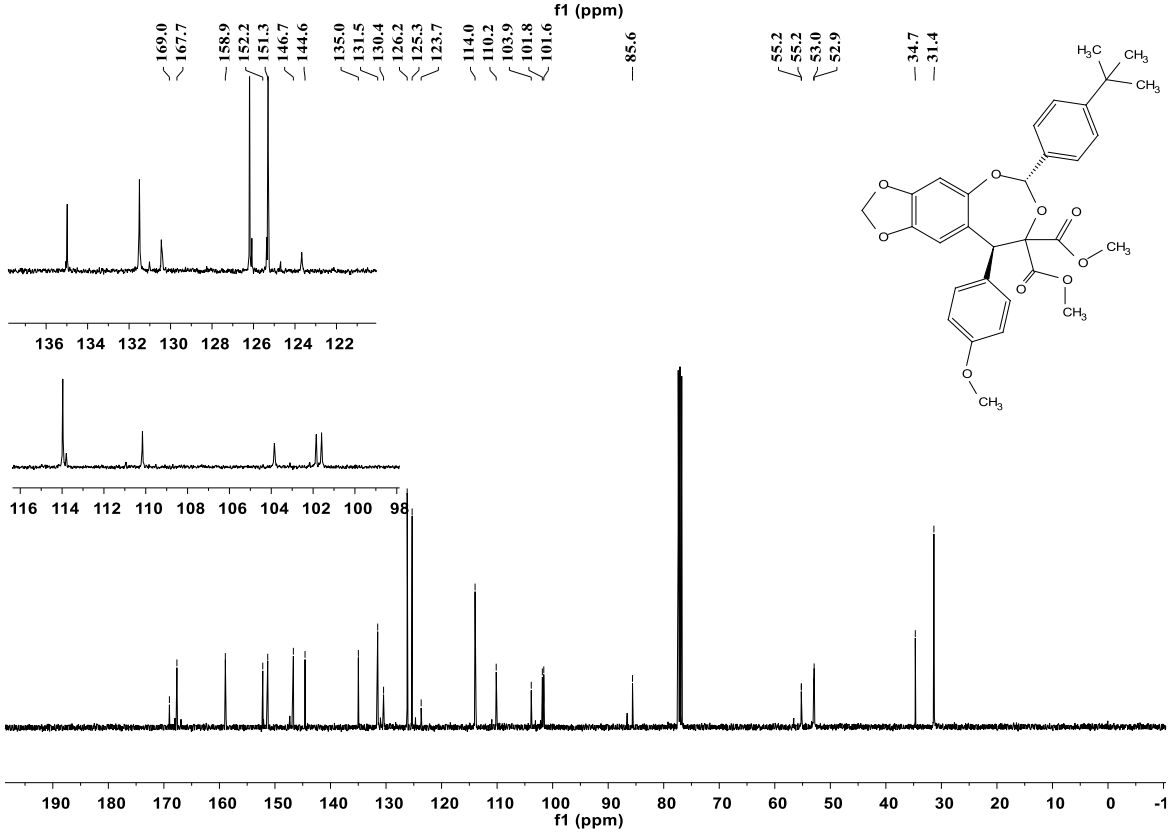


Dimethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(o-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ac):

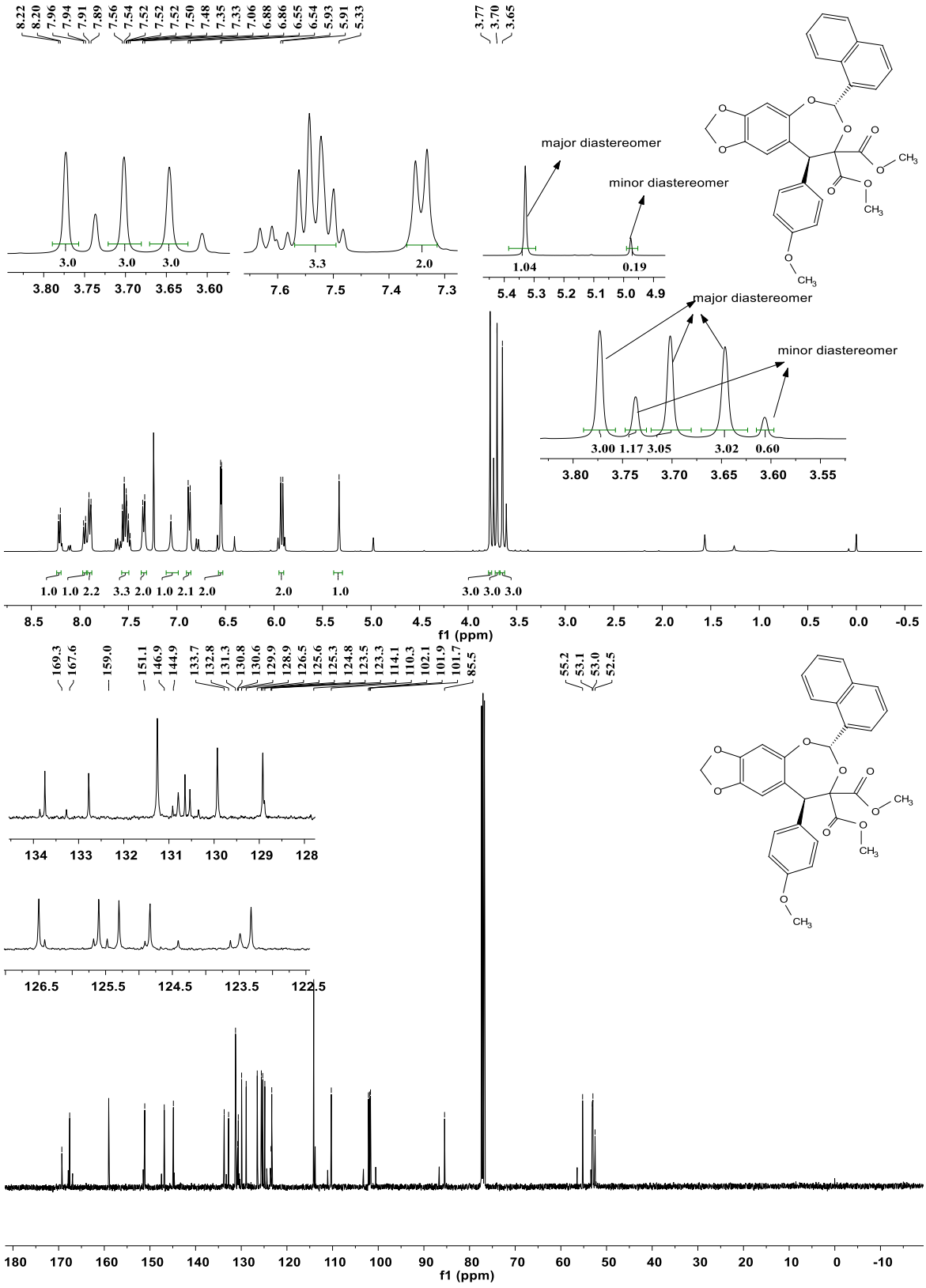


Dimethyl (*2S,5S*)-6-(4-(tert-butyl)phenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ad):

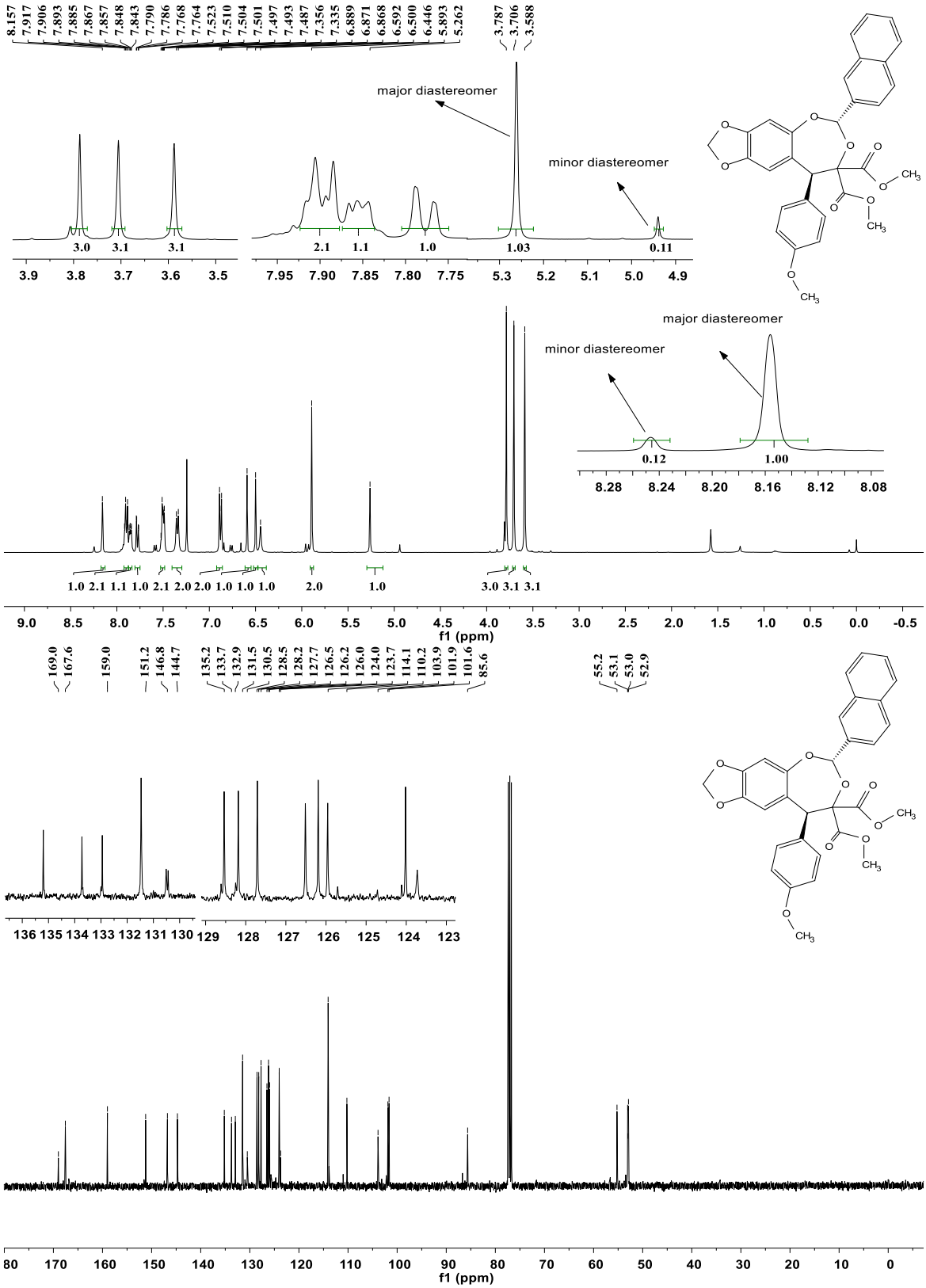




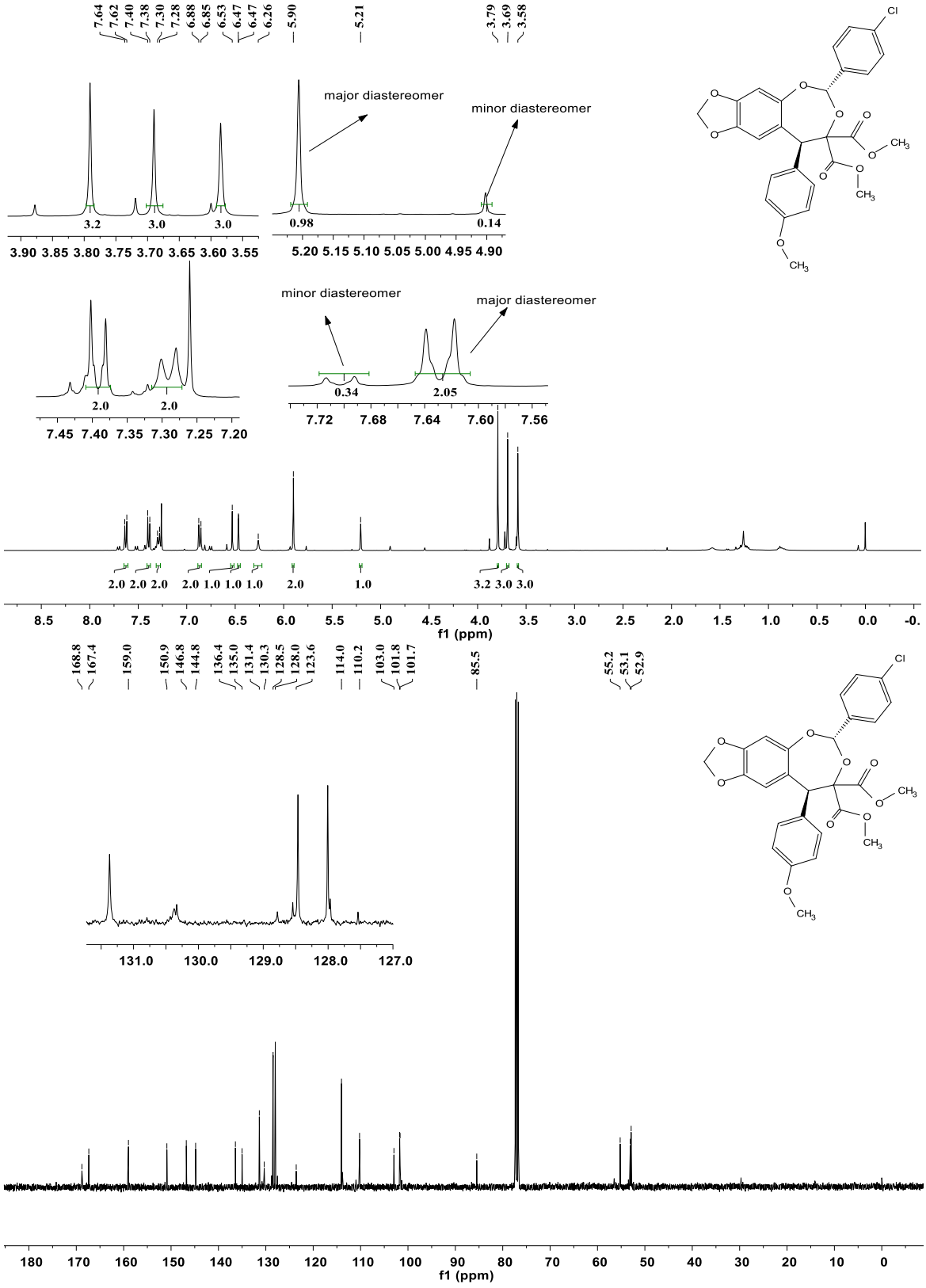
Dimethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(naphthalen-1-yl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ae):



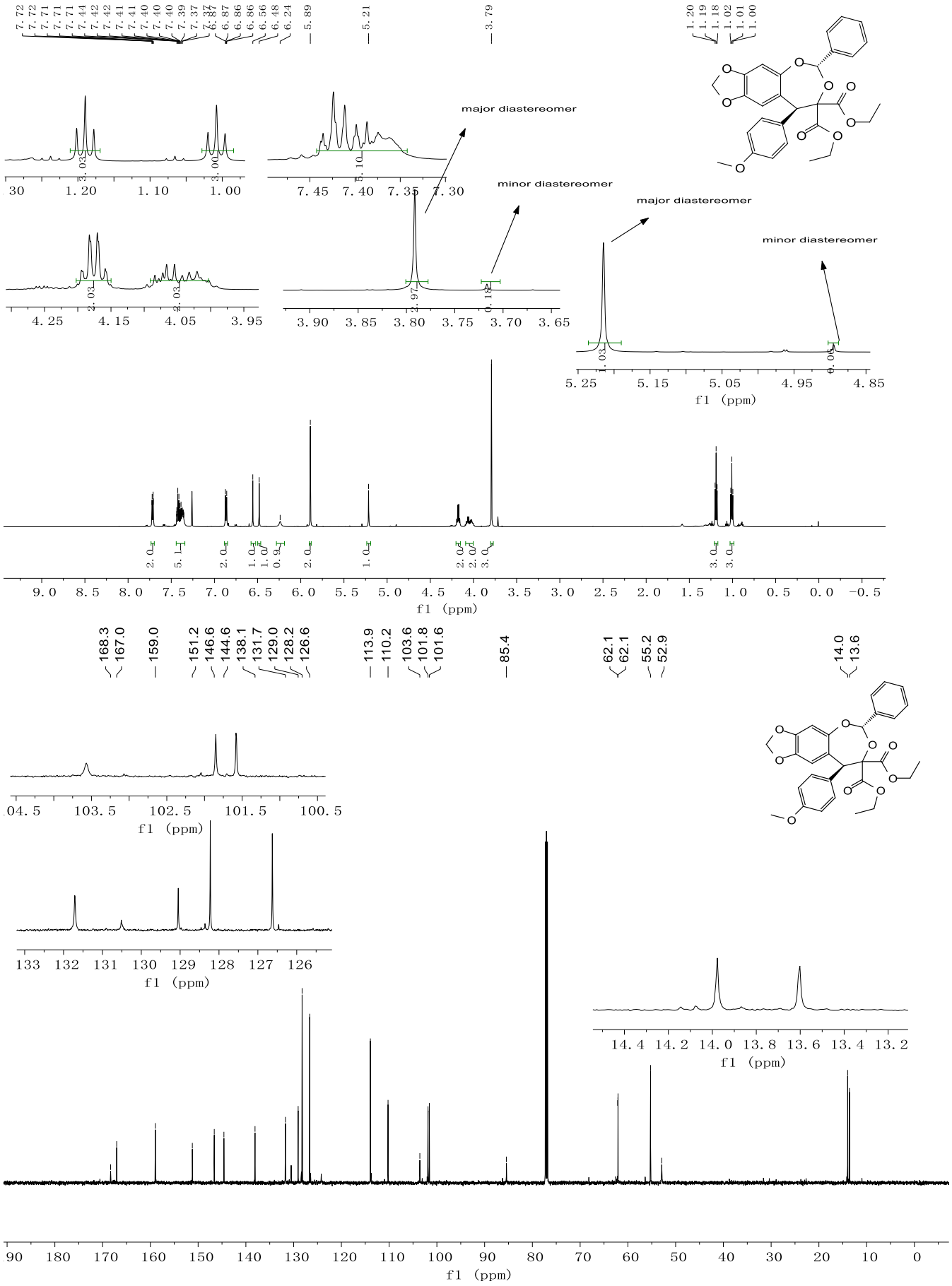
Dimethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(naphthalen-2-yl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3af):



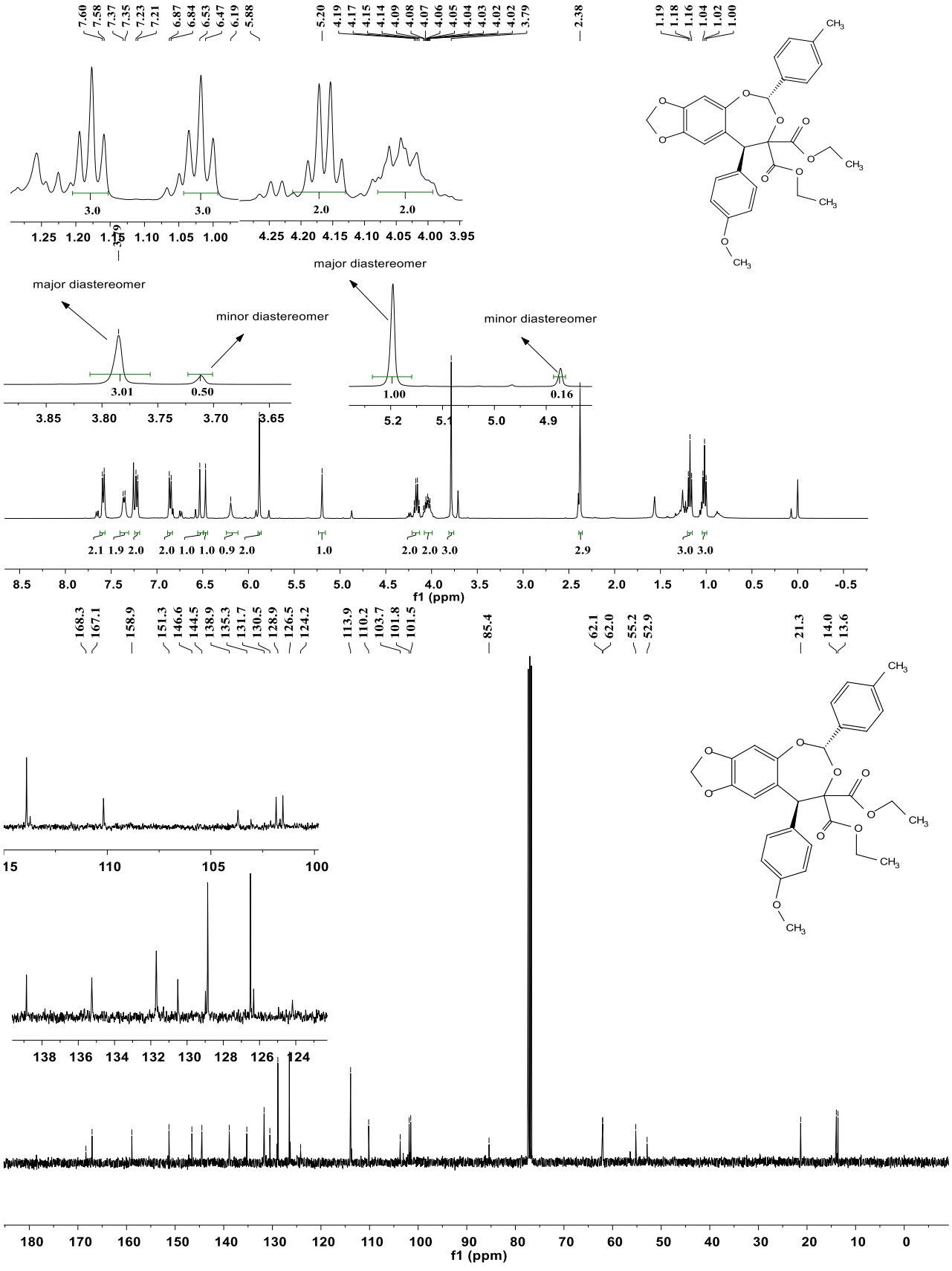
Dimethyl (*2S,5S*)-6-(4-chlorophenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ag):



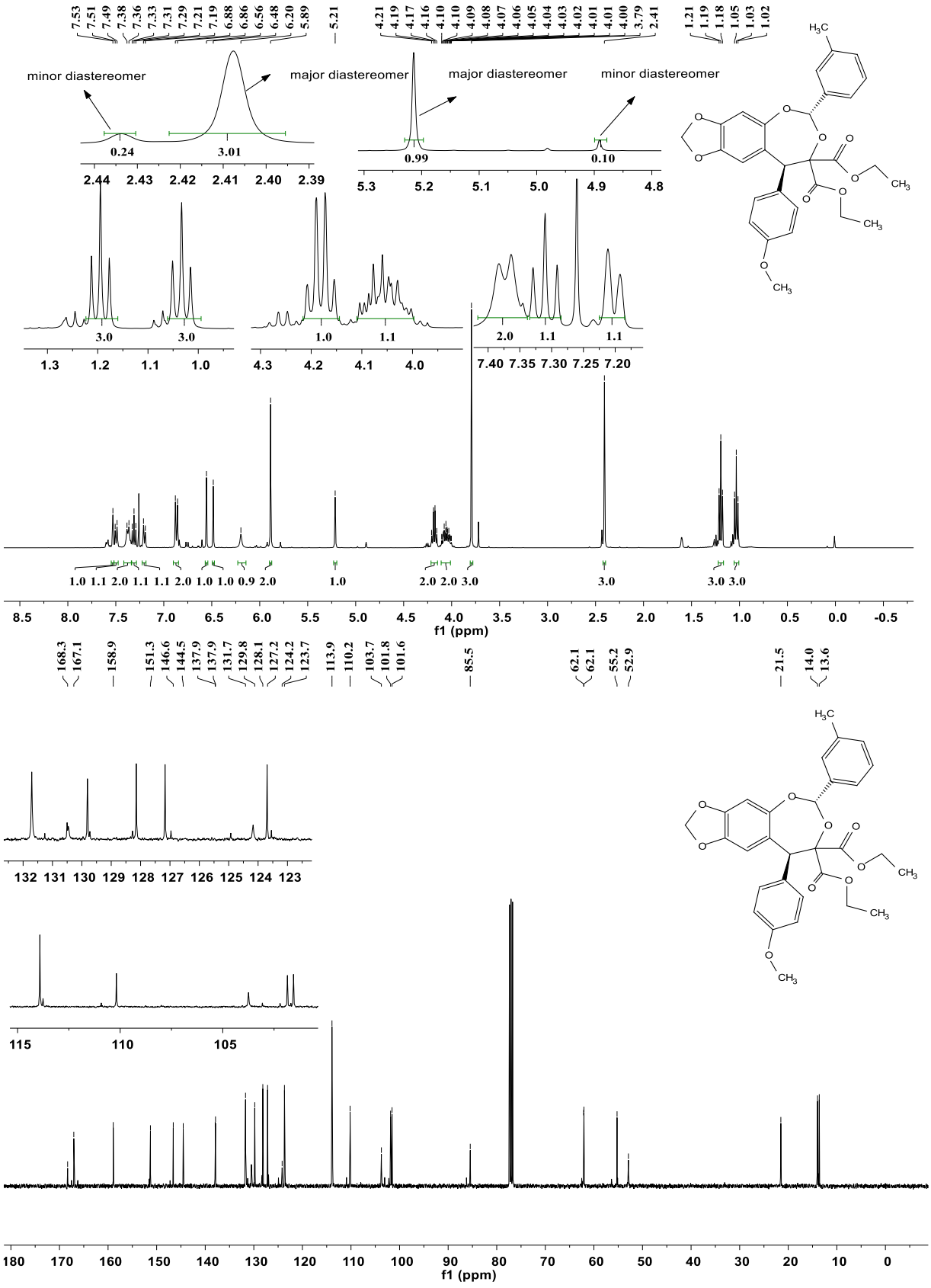
Diethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-phenyl-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ah):



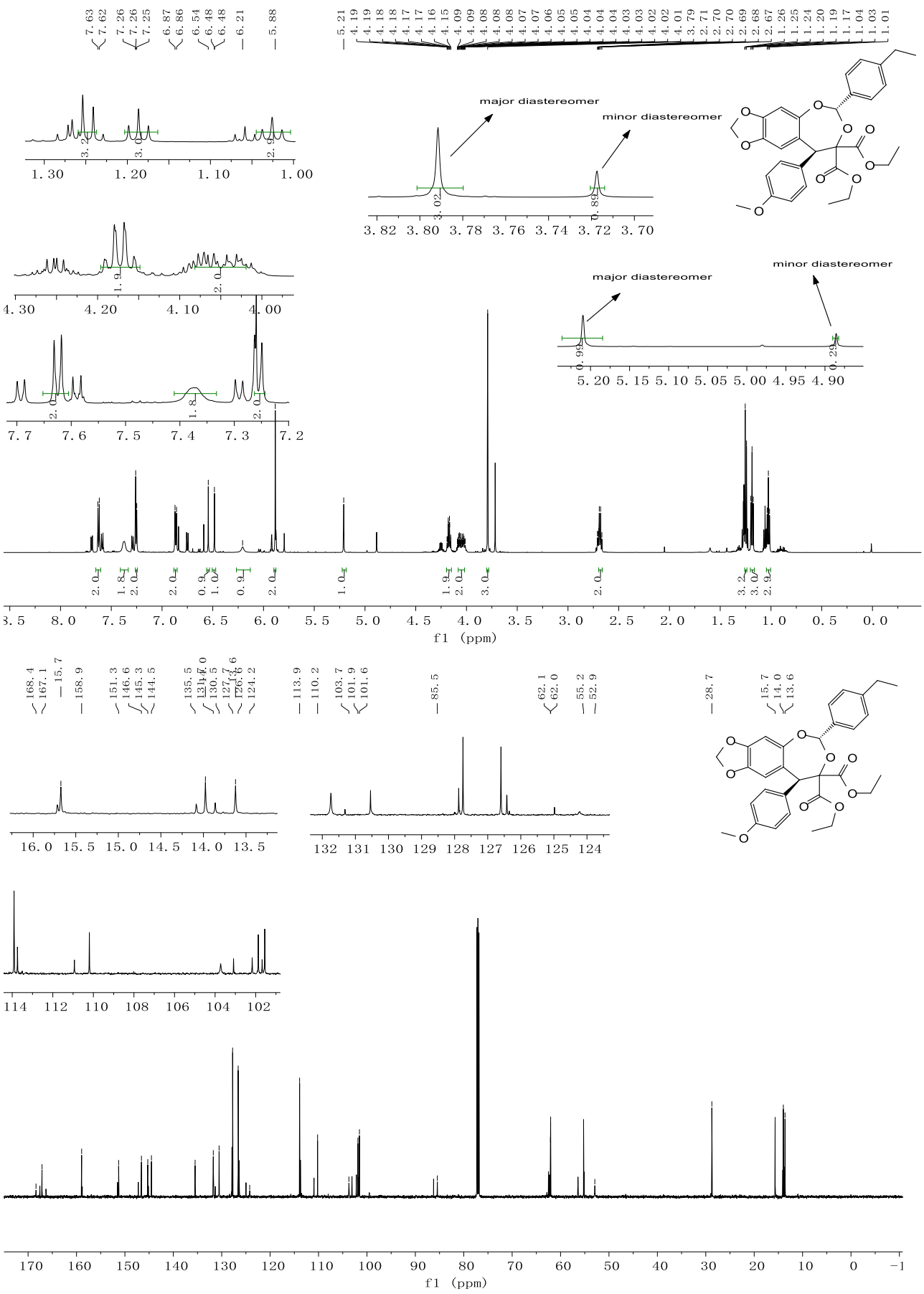
Diethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(p-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate(3ai):



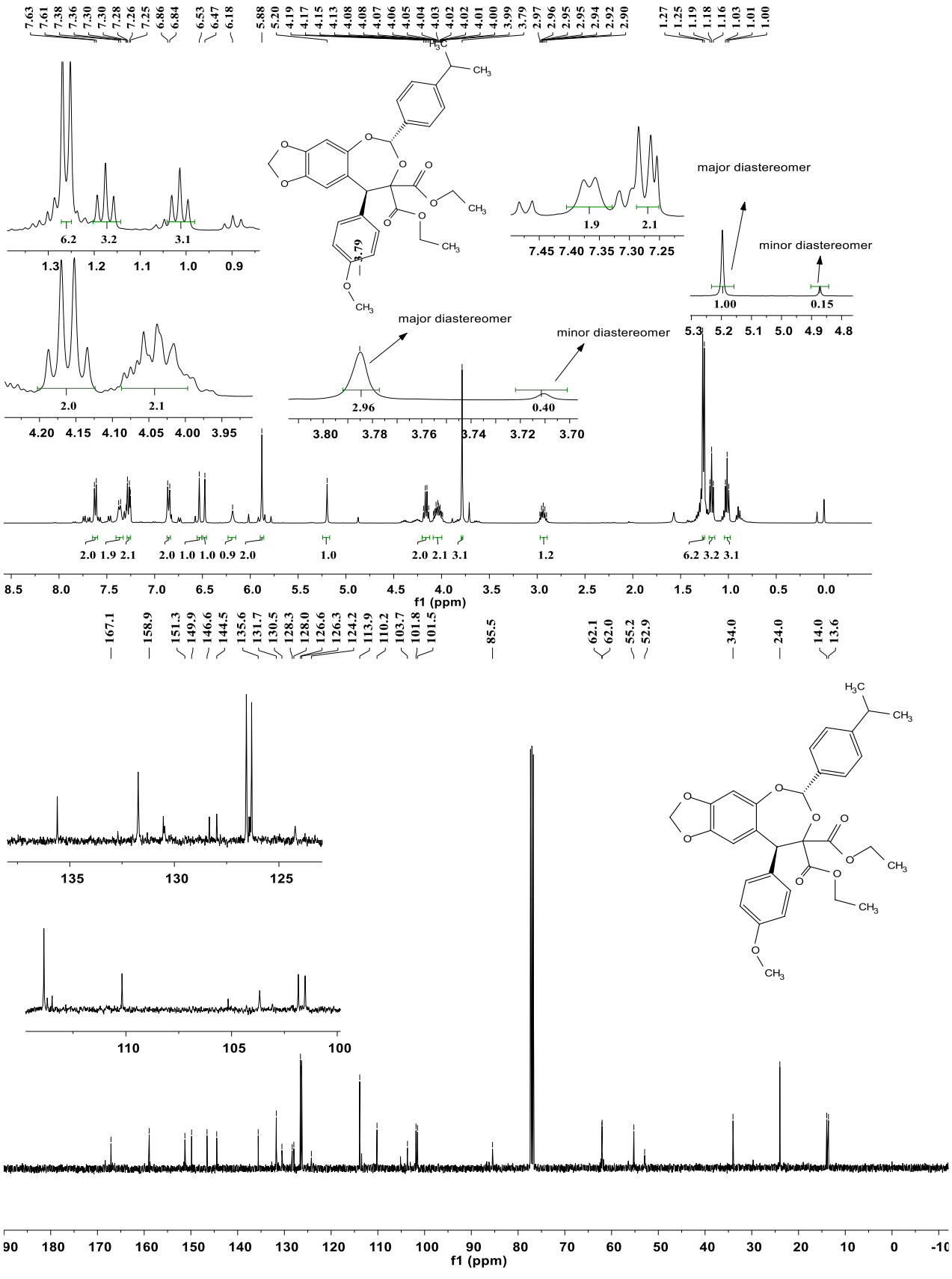
Diethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(m-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3aj):



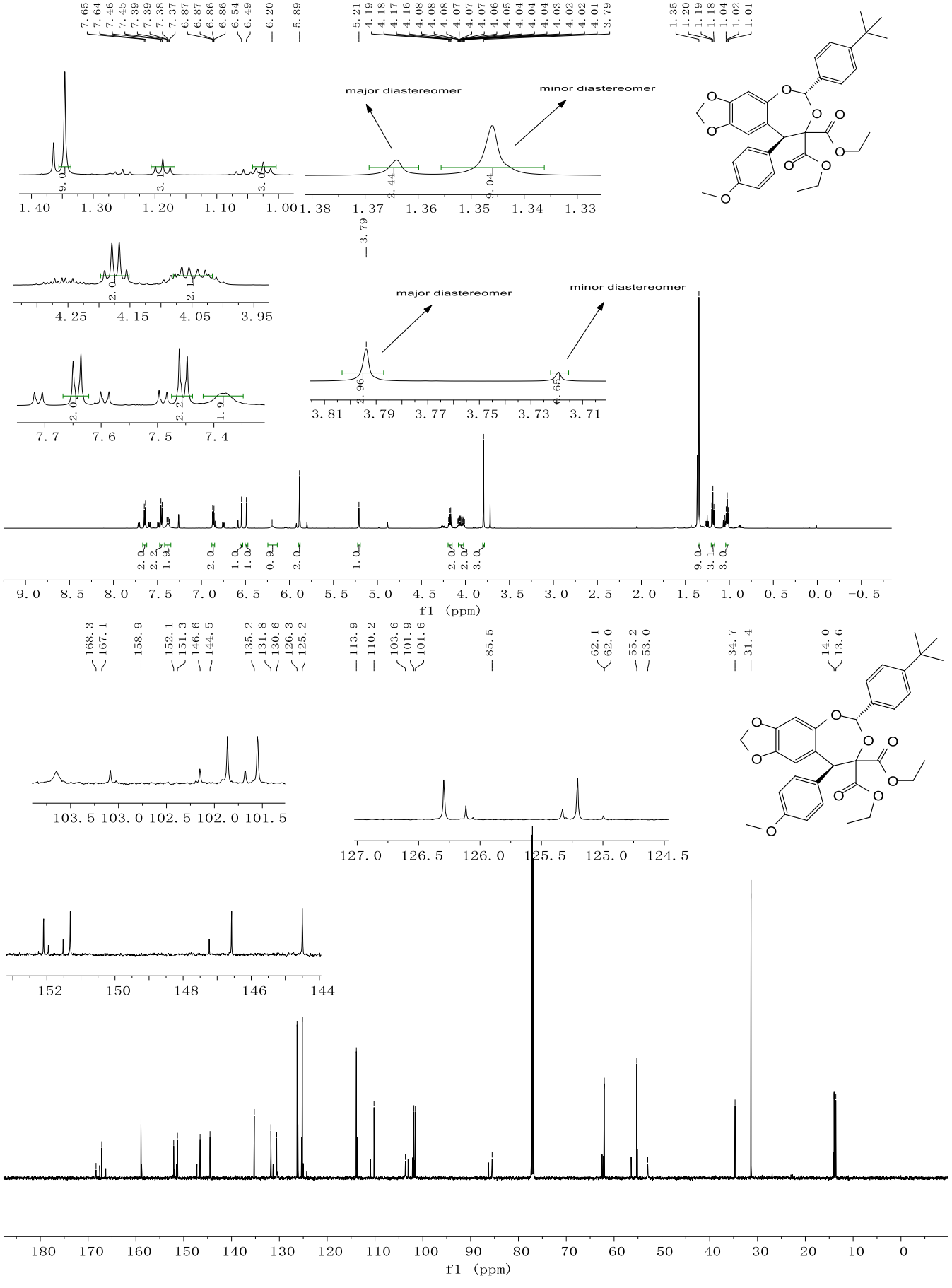
Diethyl (*2S,5S*)-6-(4-ethylphenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ak):



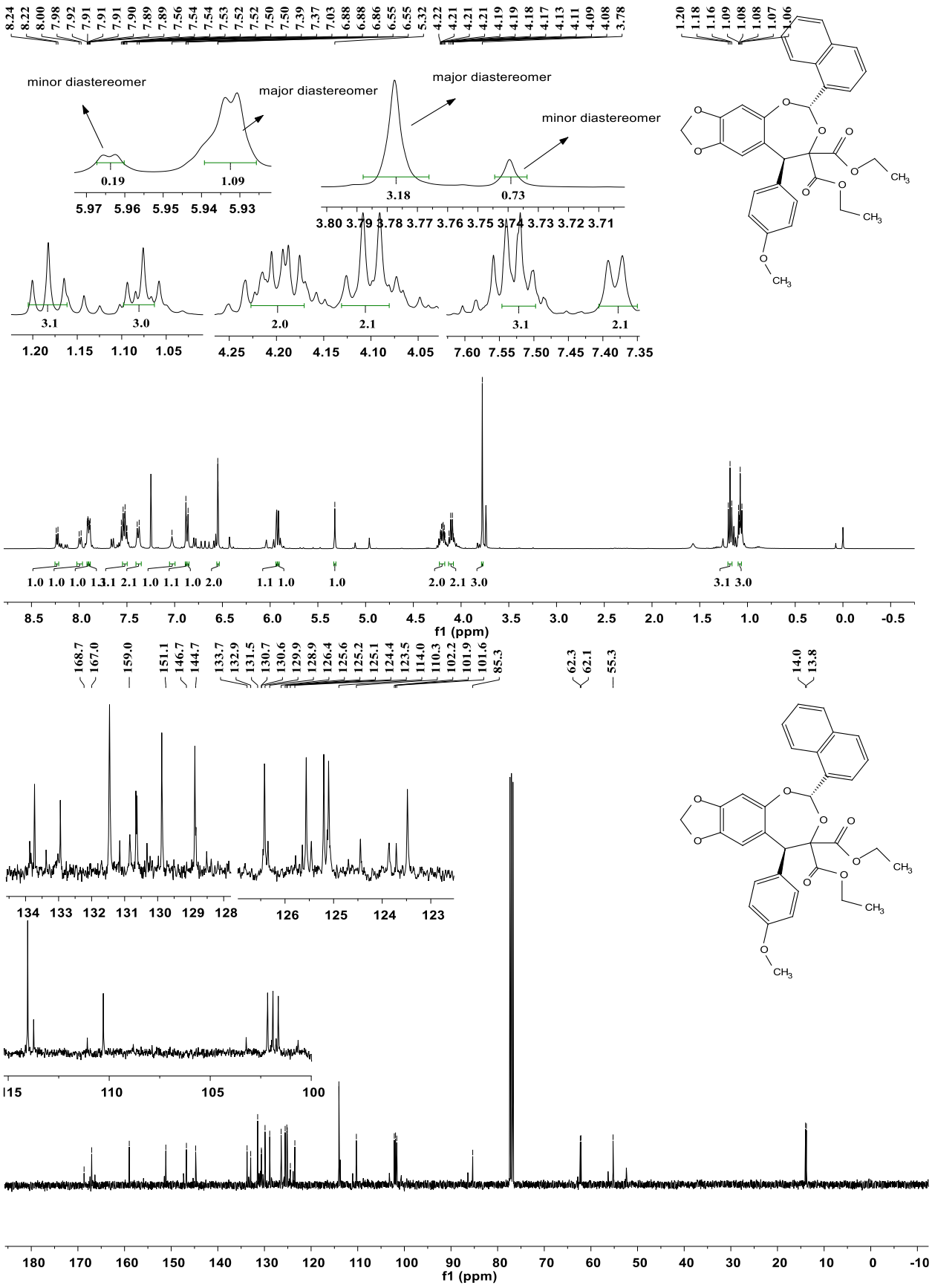
Diethyl (*2S,5S*)-6-(4-isopropylphenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3al):



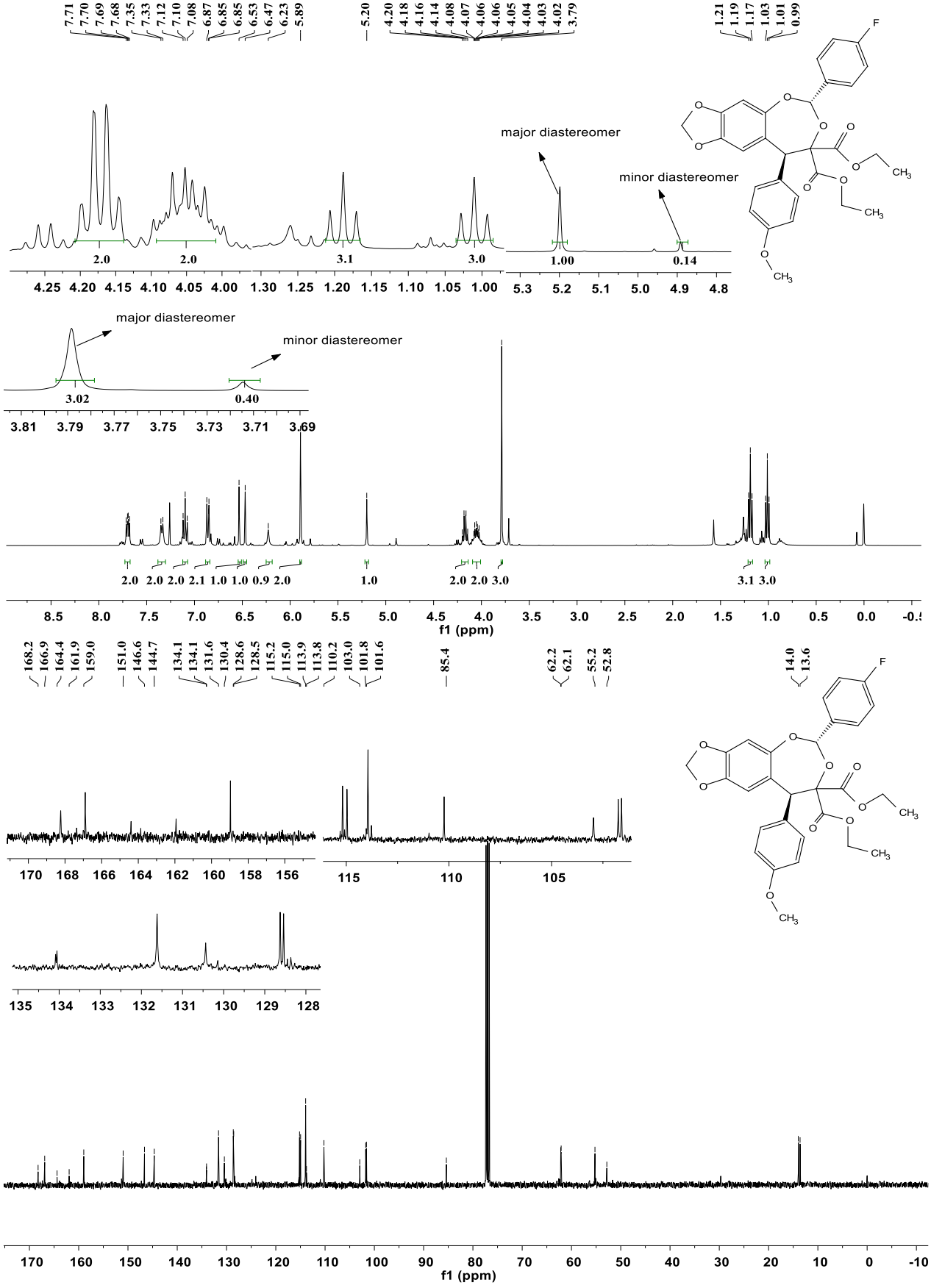
Diethyl (*2S,5S*)-6-(4-(tert-butyl)phenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3am):

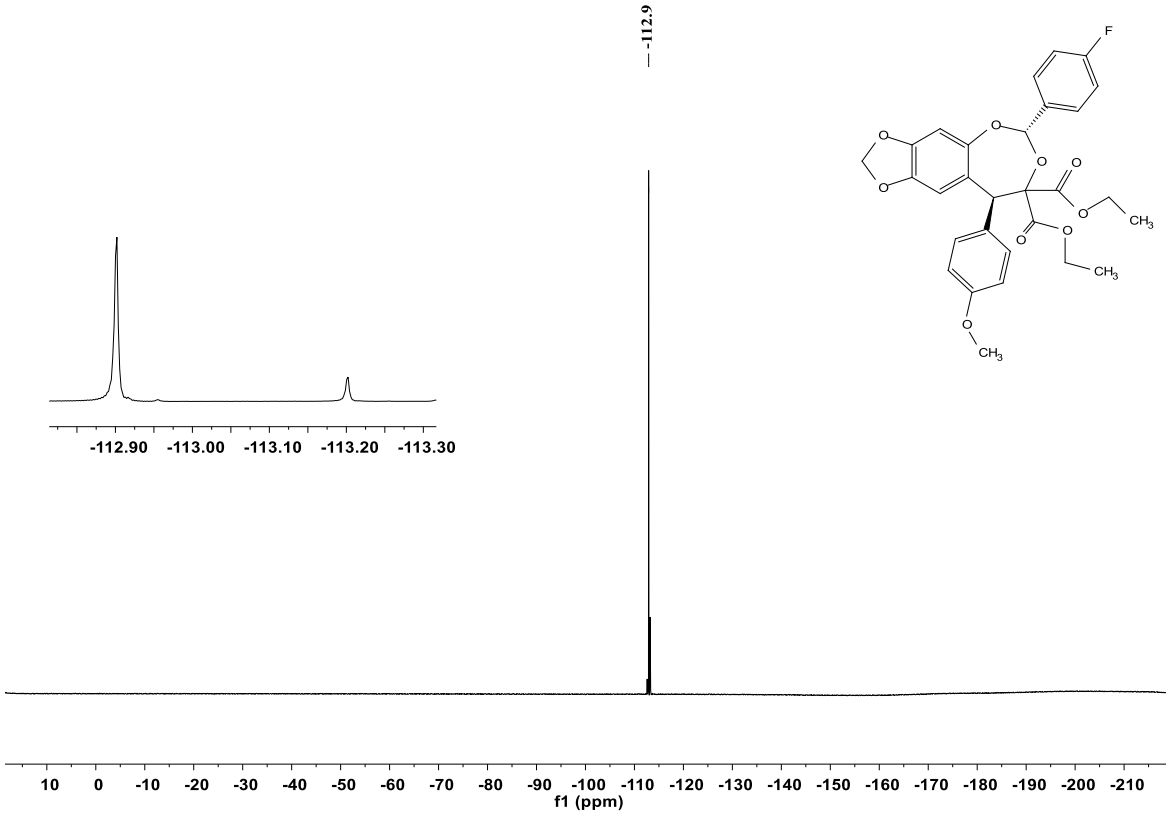


Diethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(naphthalen-1-yl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3an):

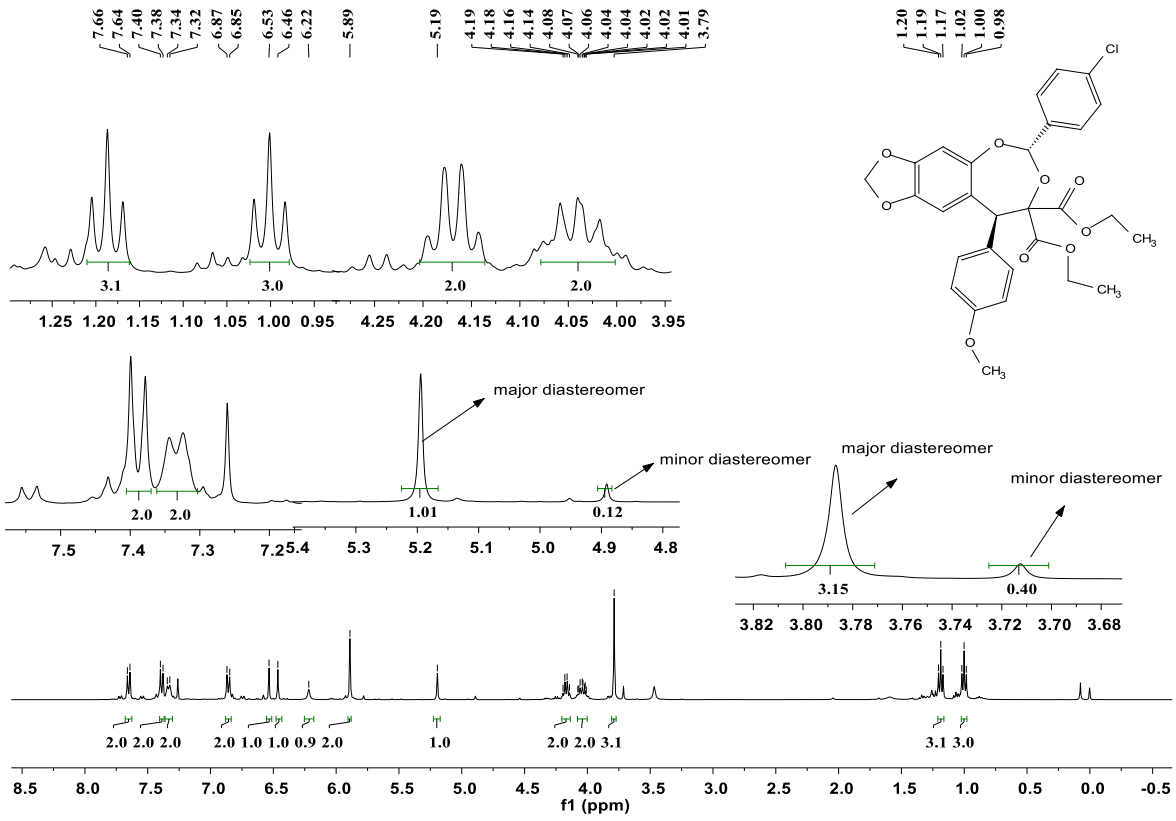


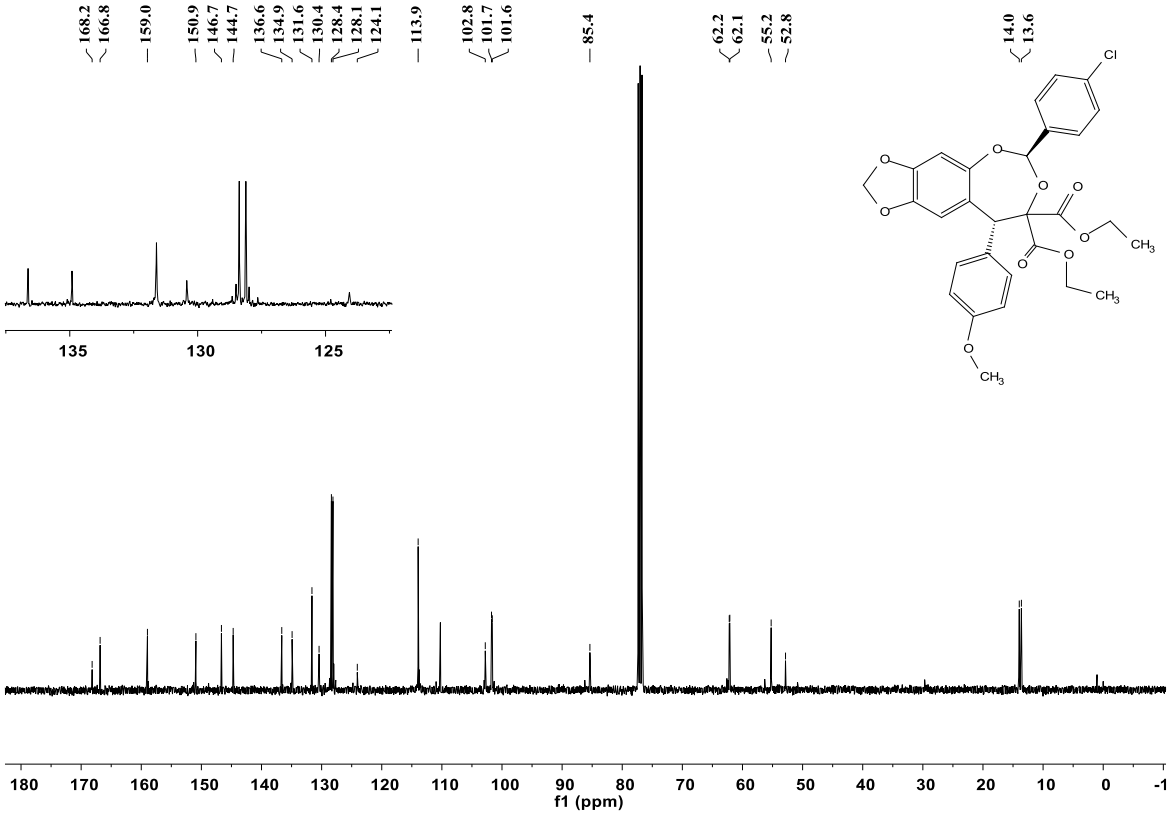
Diethyl (*2S,5S*)-6-(4-fluorophenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ao):



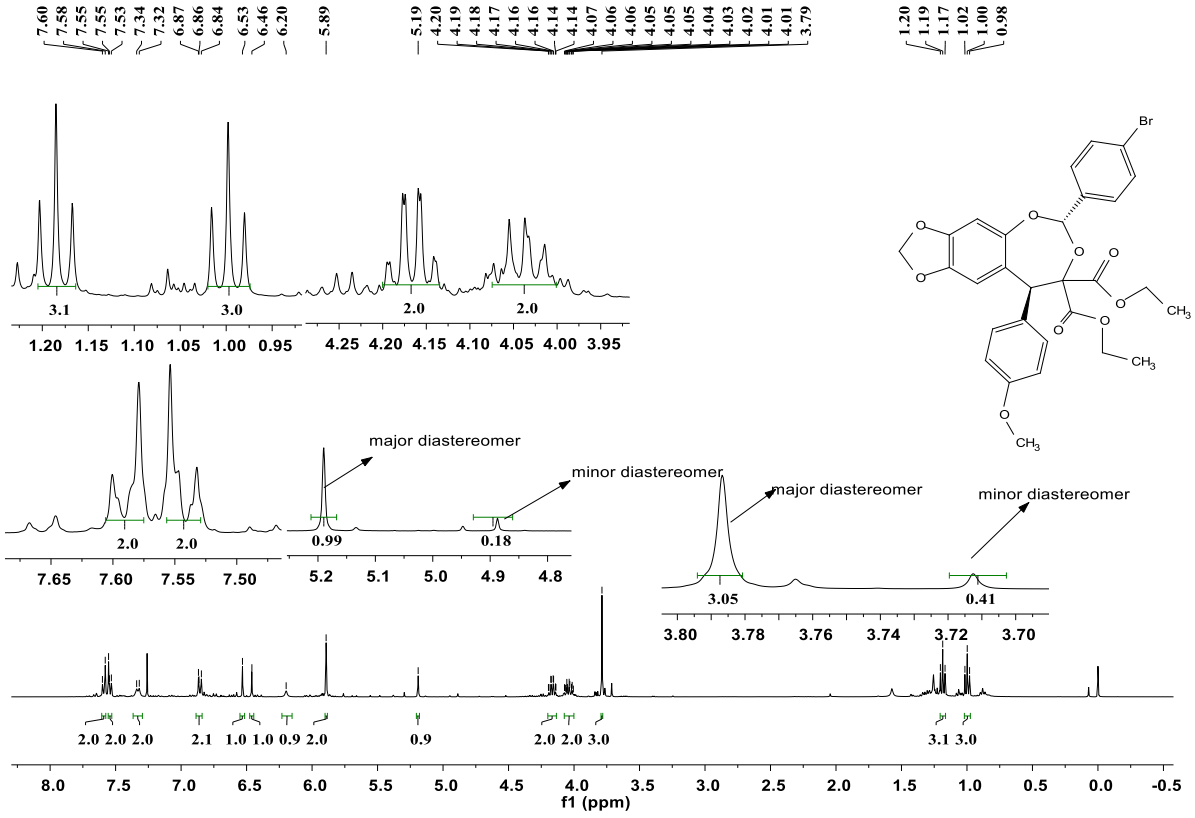


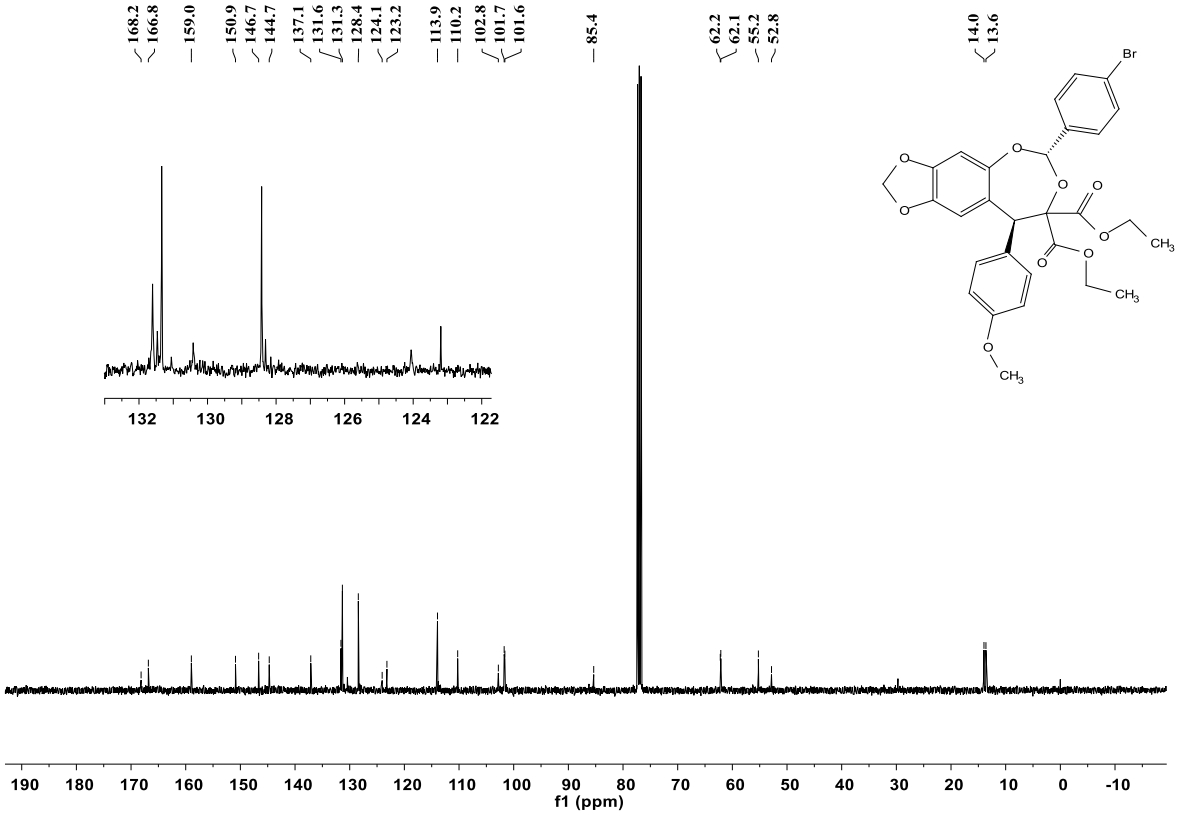
Diethyl (*2S,5S*)-6-(4-chlorophenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ap):



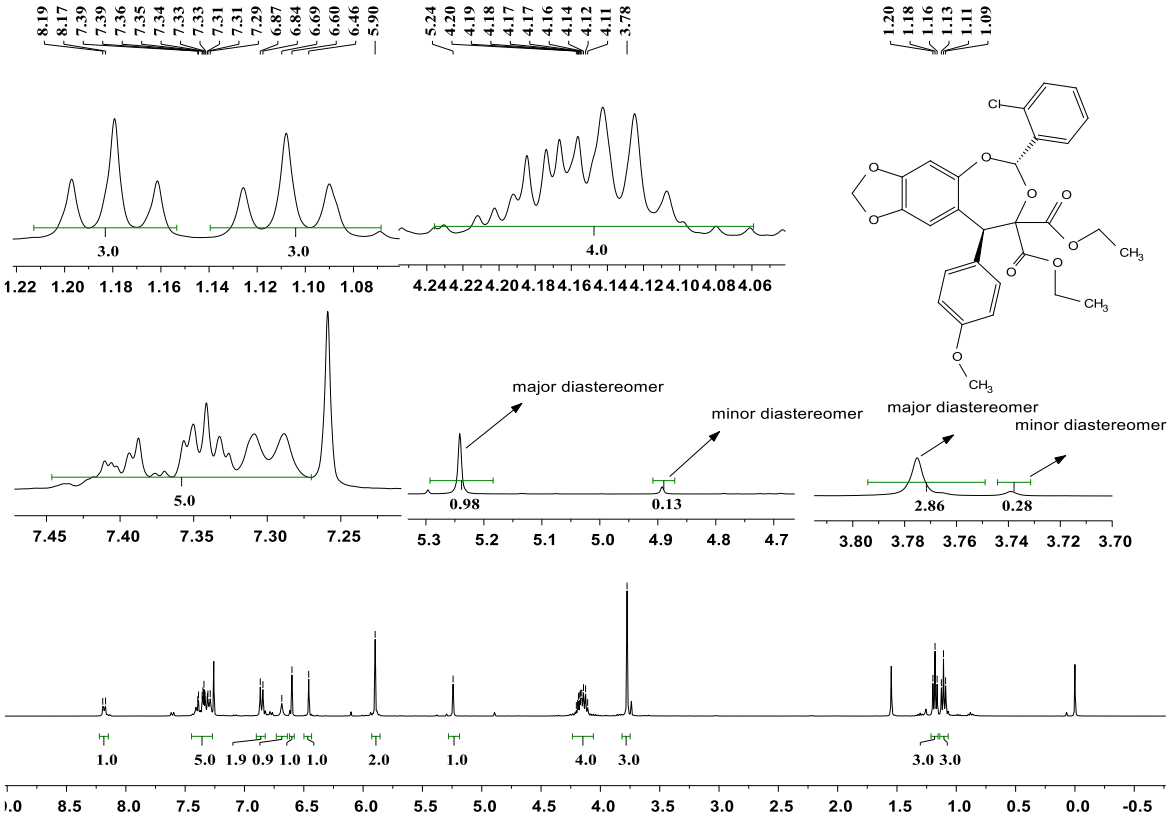


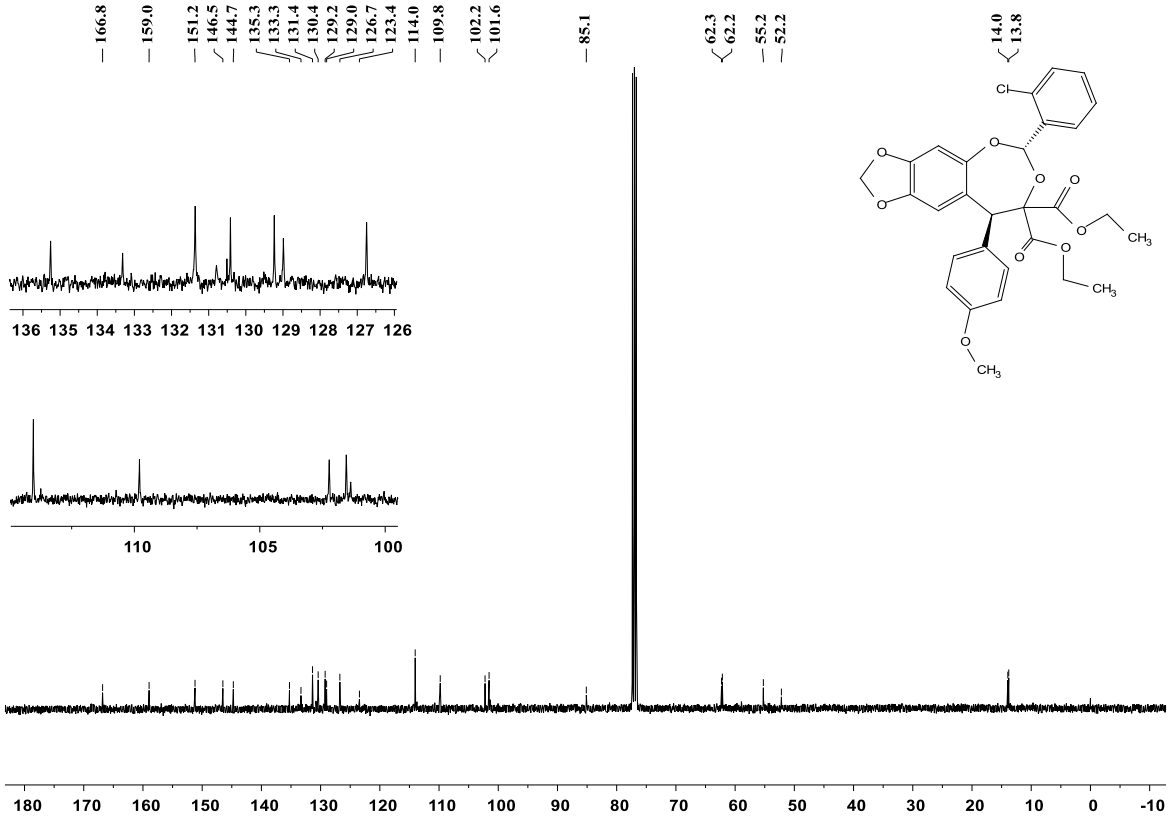
Diethyl (*2S,5S*)-6-(4-bromophenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3aq):



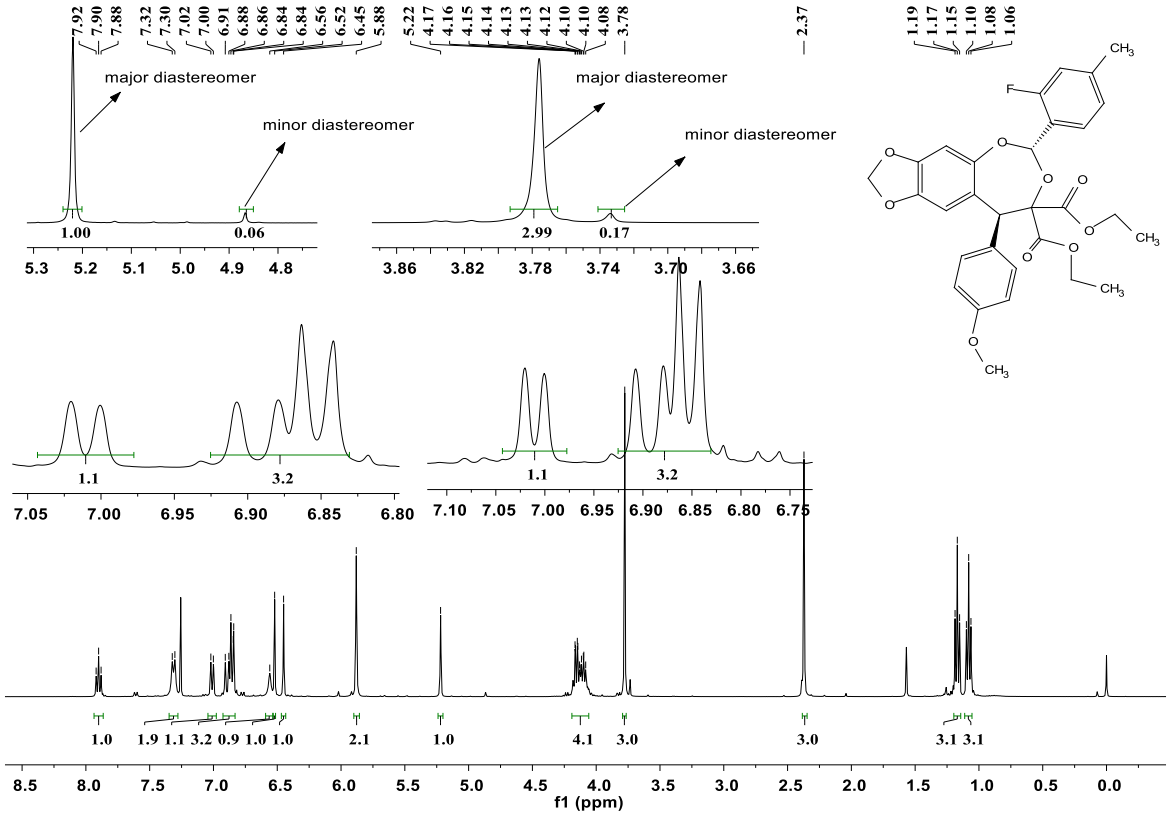


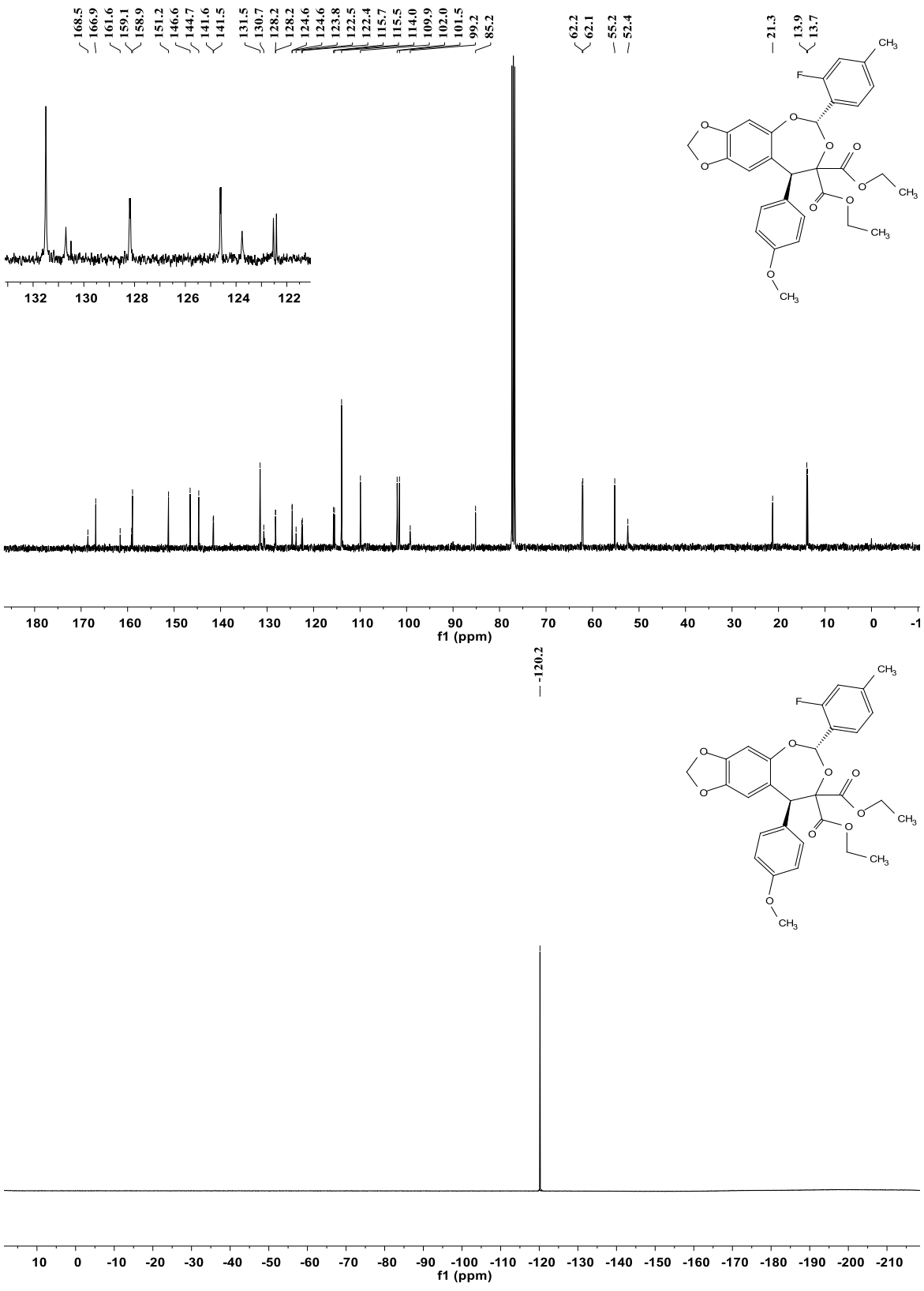
Diethyl (*2S,5S*)-6-(2-chlorophenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ar):



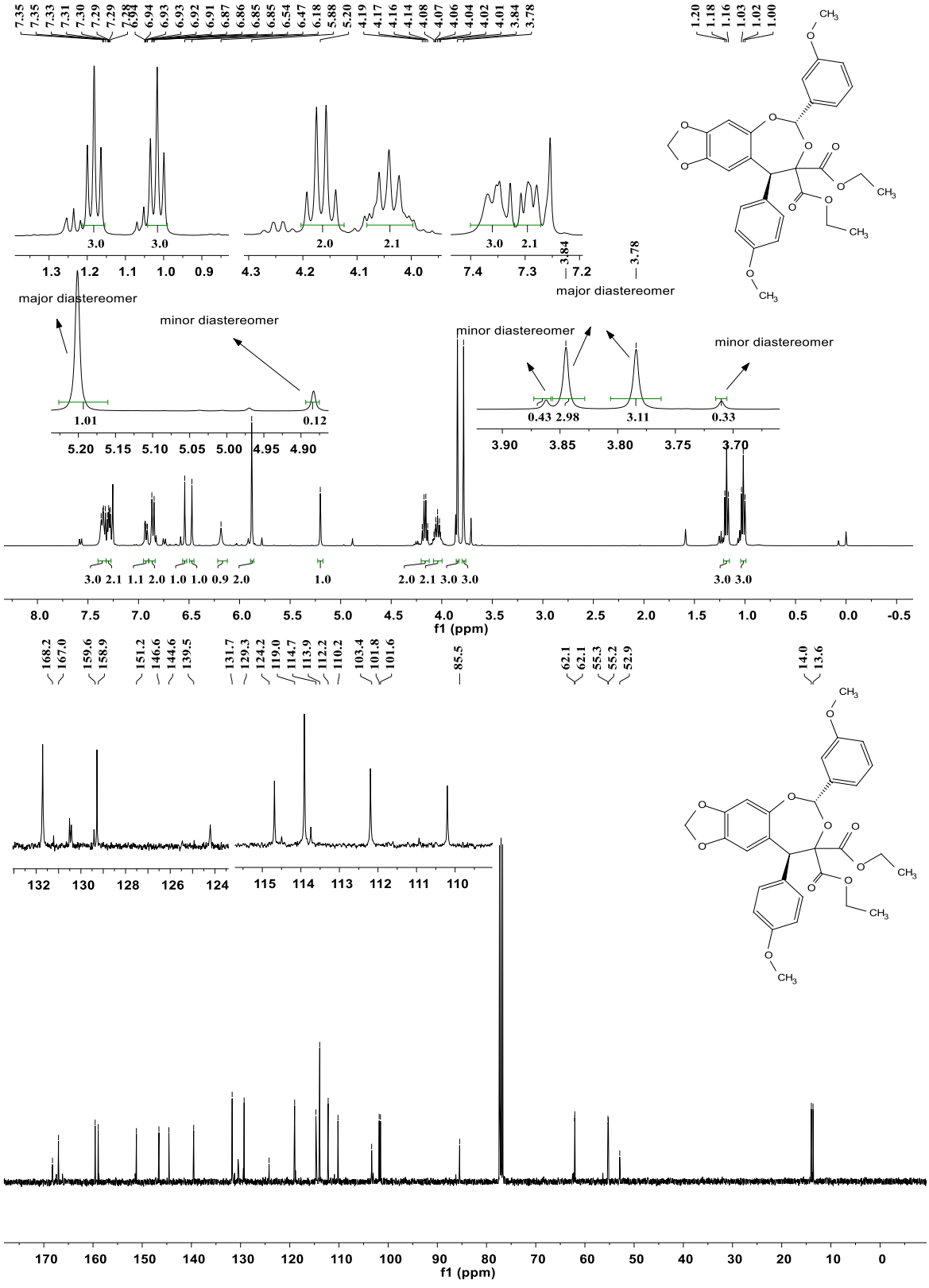


Diethyl (*2S,5S*)-6-(2-fluoro-4-methylphenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3as):

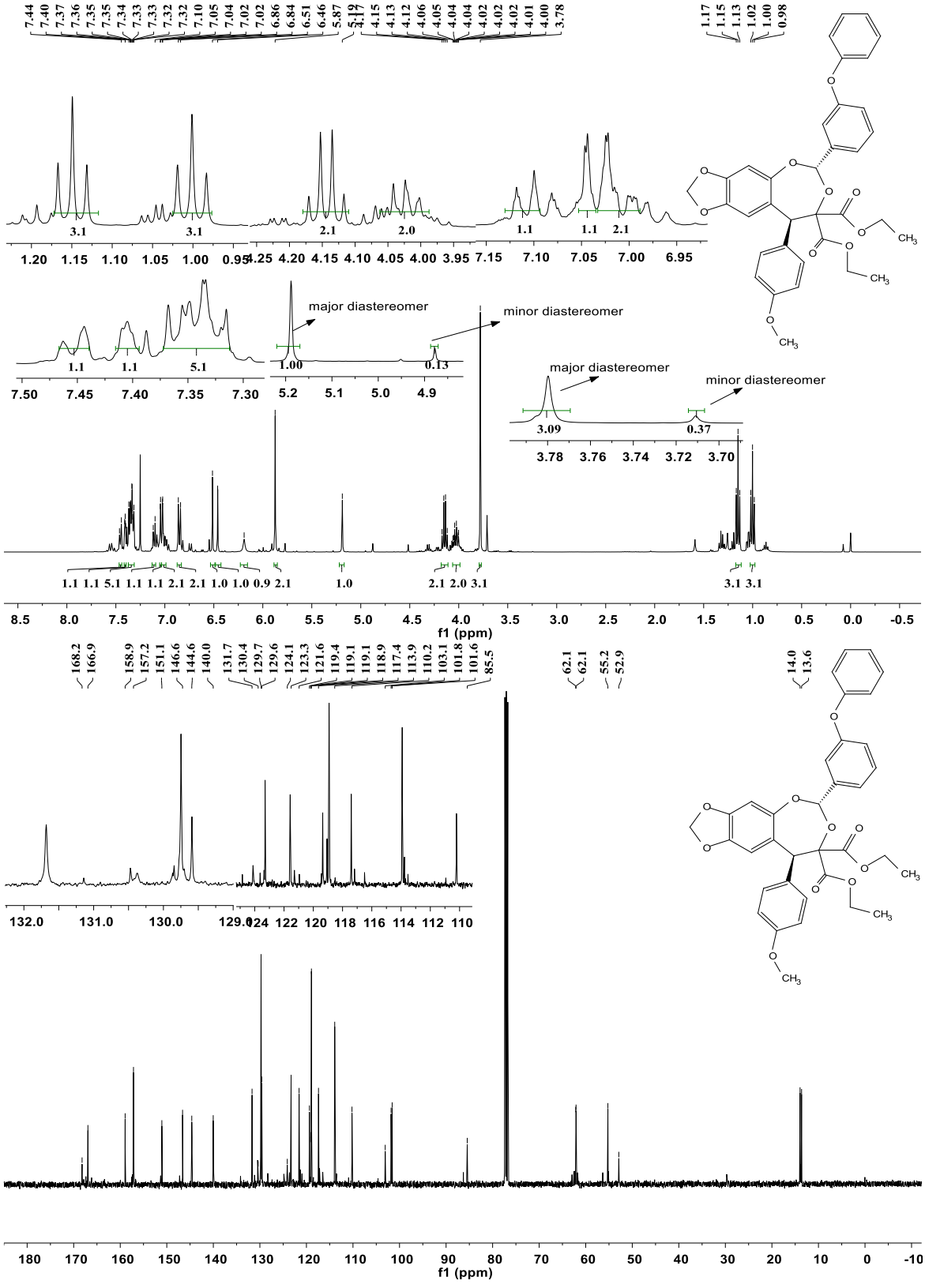




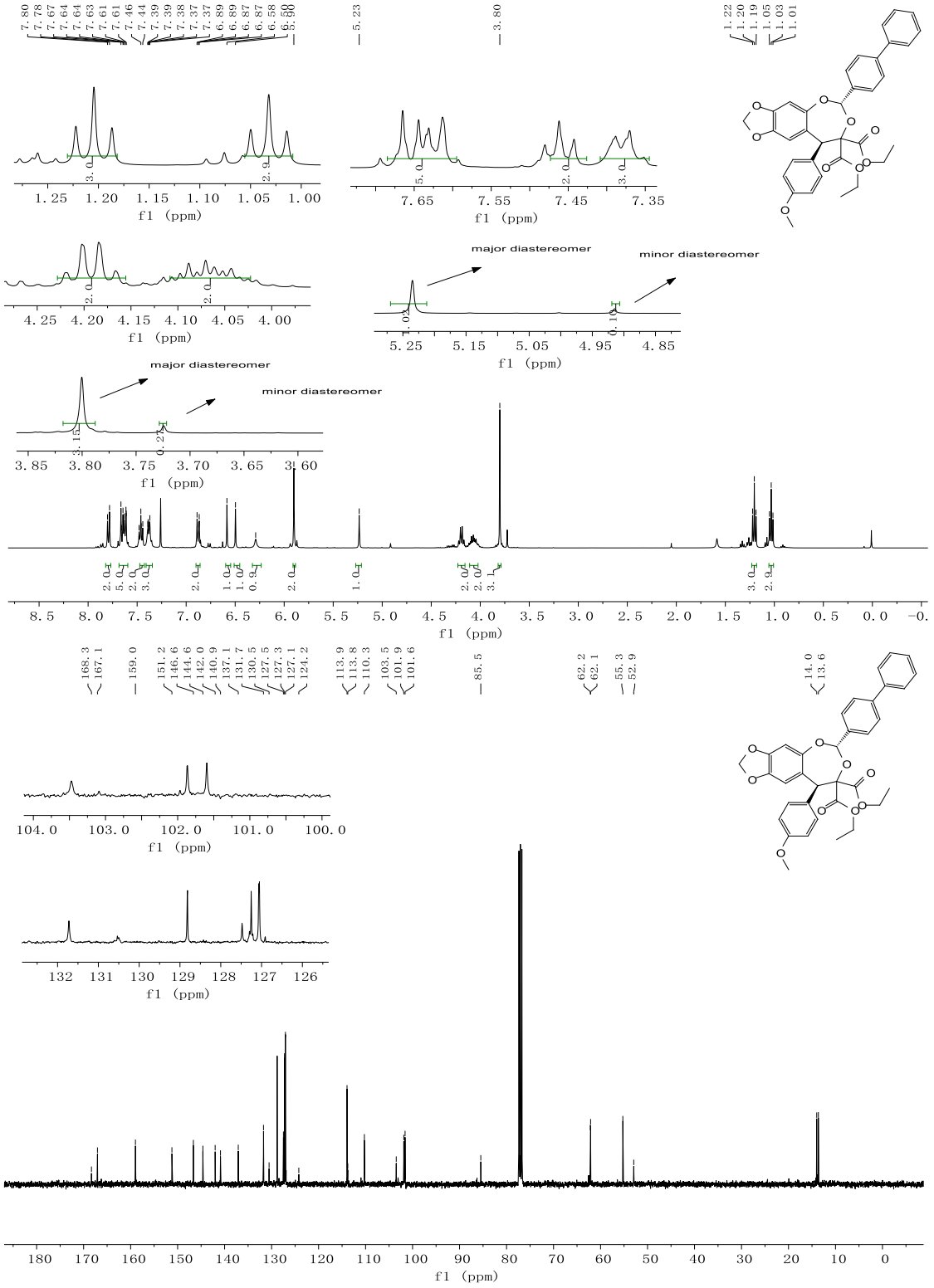
Diethyl (*2S,5S*)-6-(3-methoxyphenyl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3at):



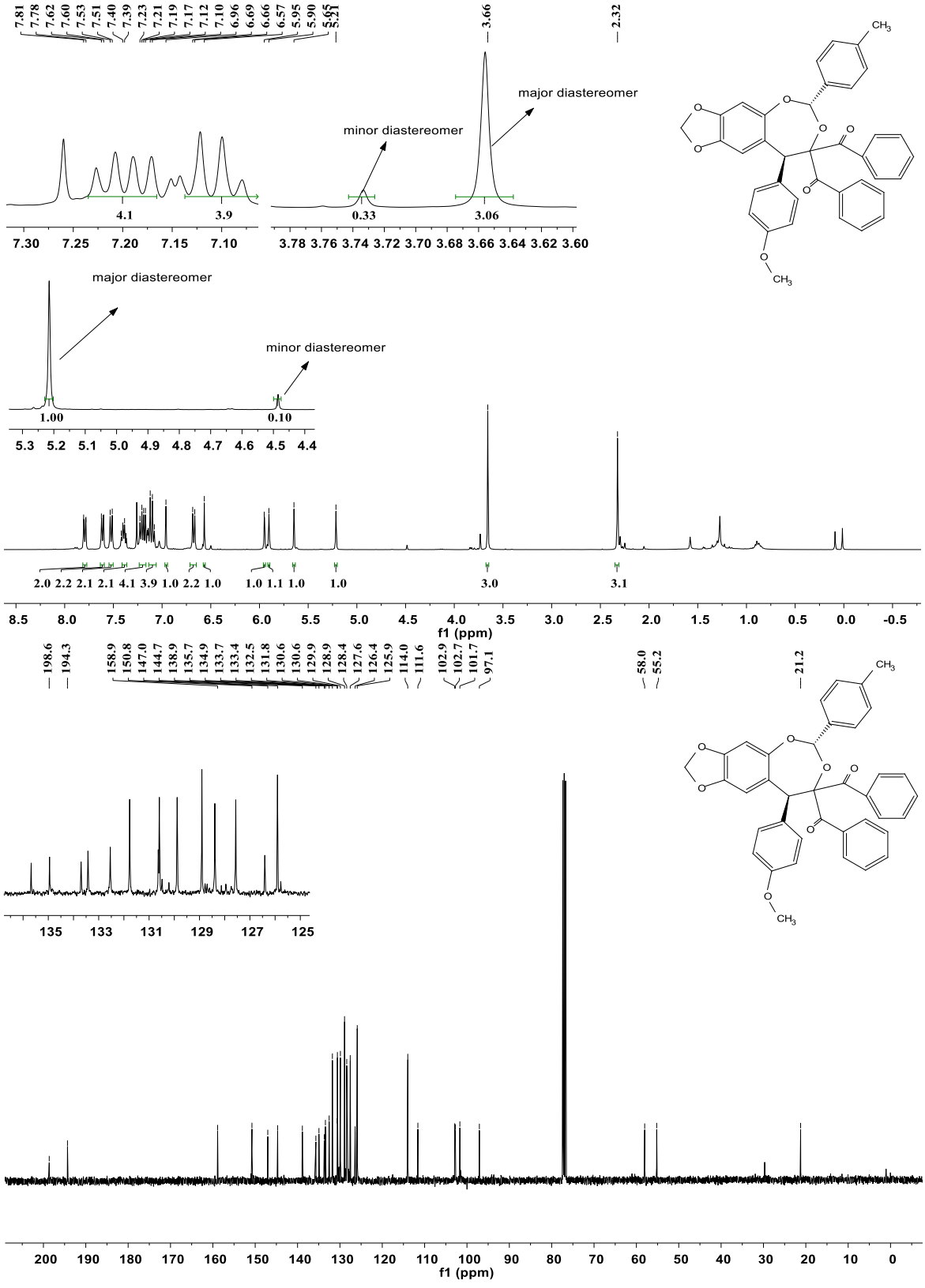
Diethyl (*2S,5S*)-9-(4-methoxyphenyl)-6-(3-phenoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3au):



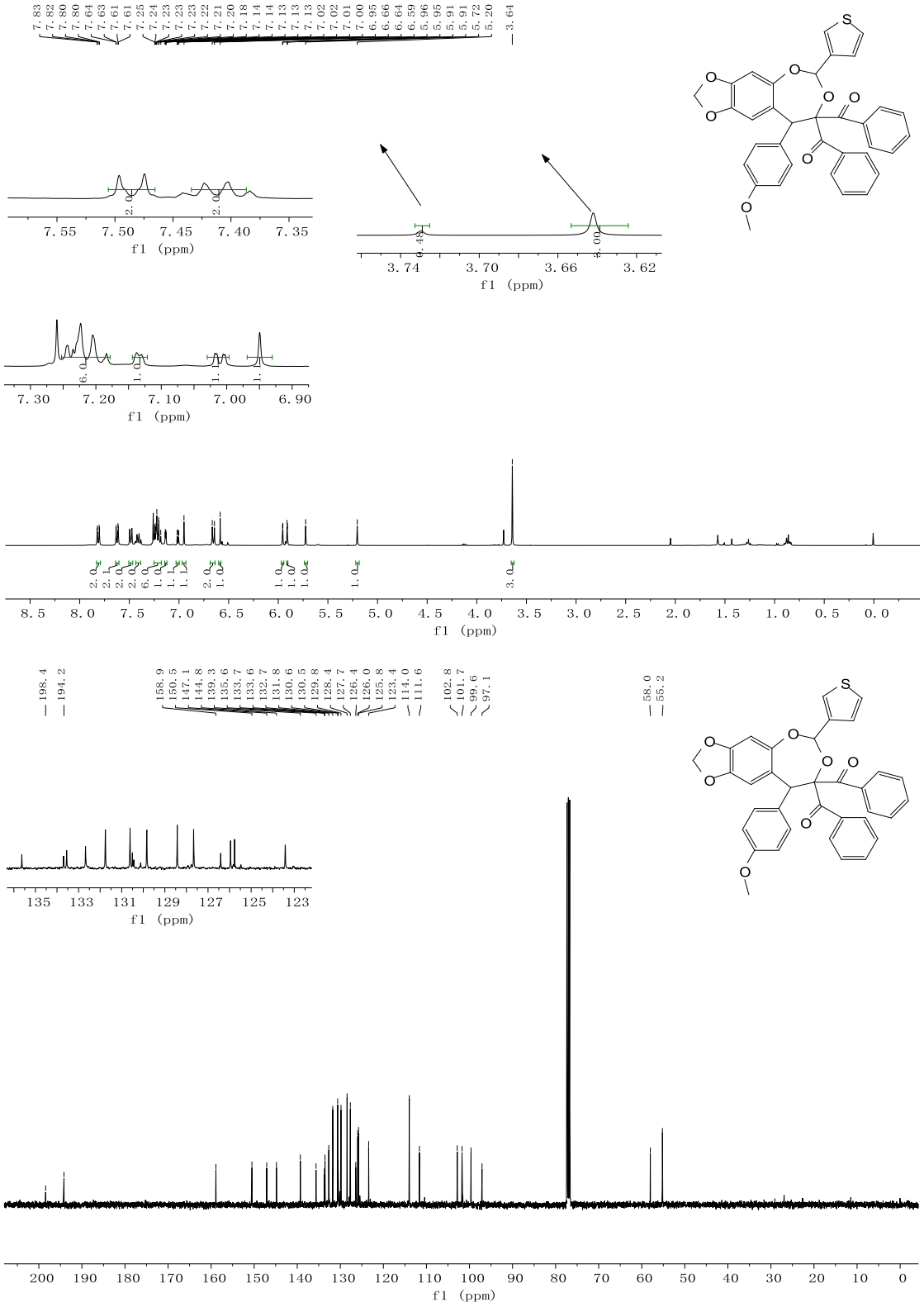
Diethyl (*2S,5S*)-6-([1,1'-biphenyl]-4-yl)-9-(4-methoxyphenyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3av)



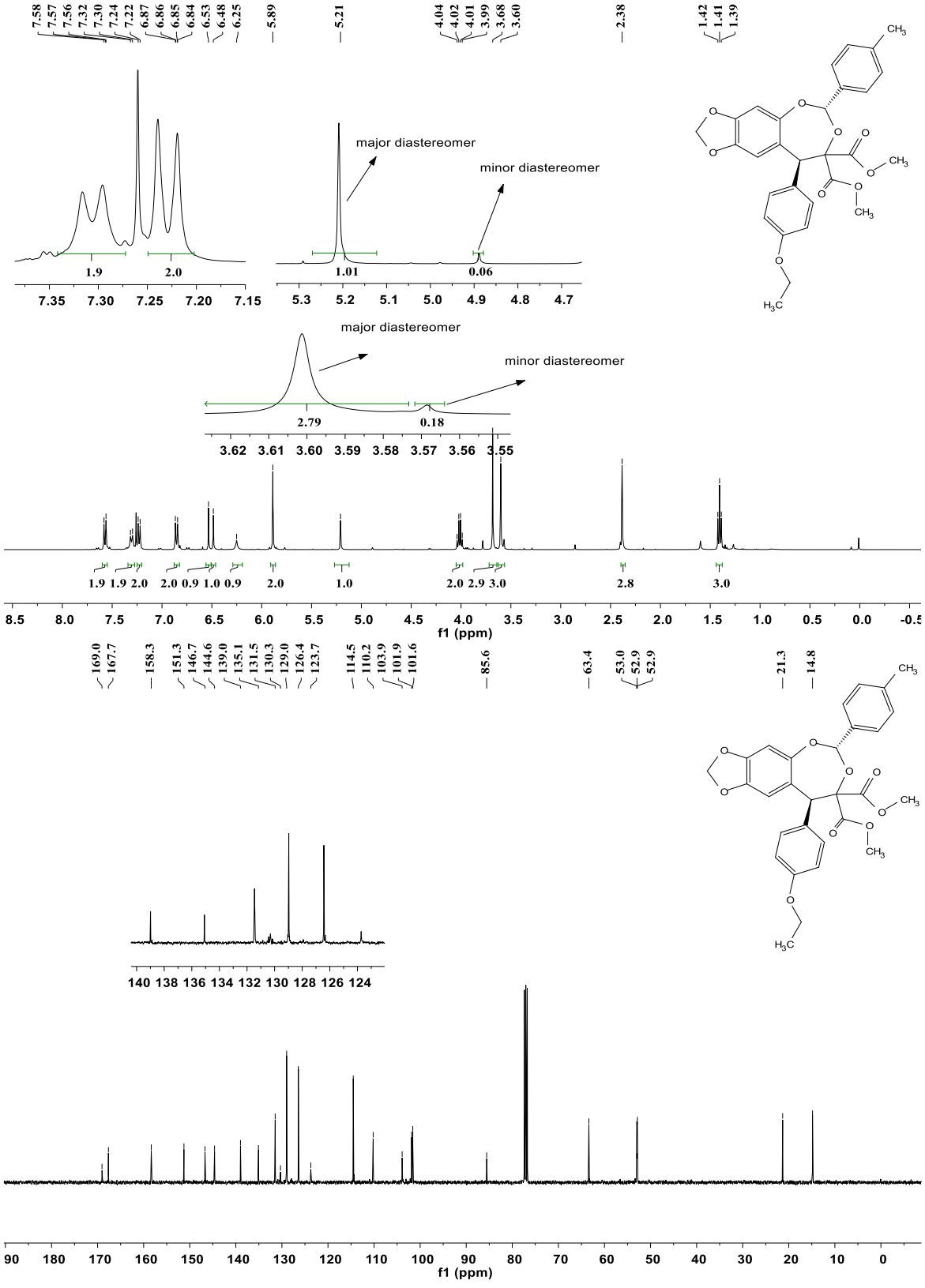
(*2S,5S*)-9-(4-methoxyphenyl)-6-(p-tolyl)-8,9-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8-diyl)bis(phenylmethanone) (3aw):



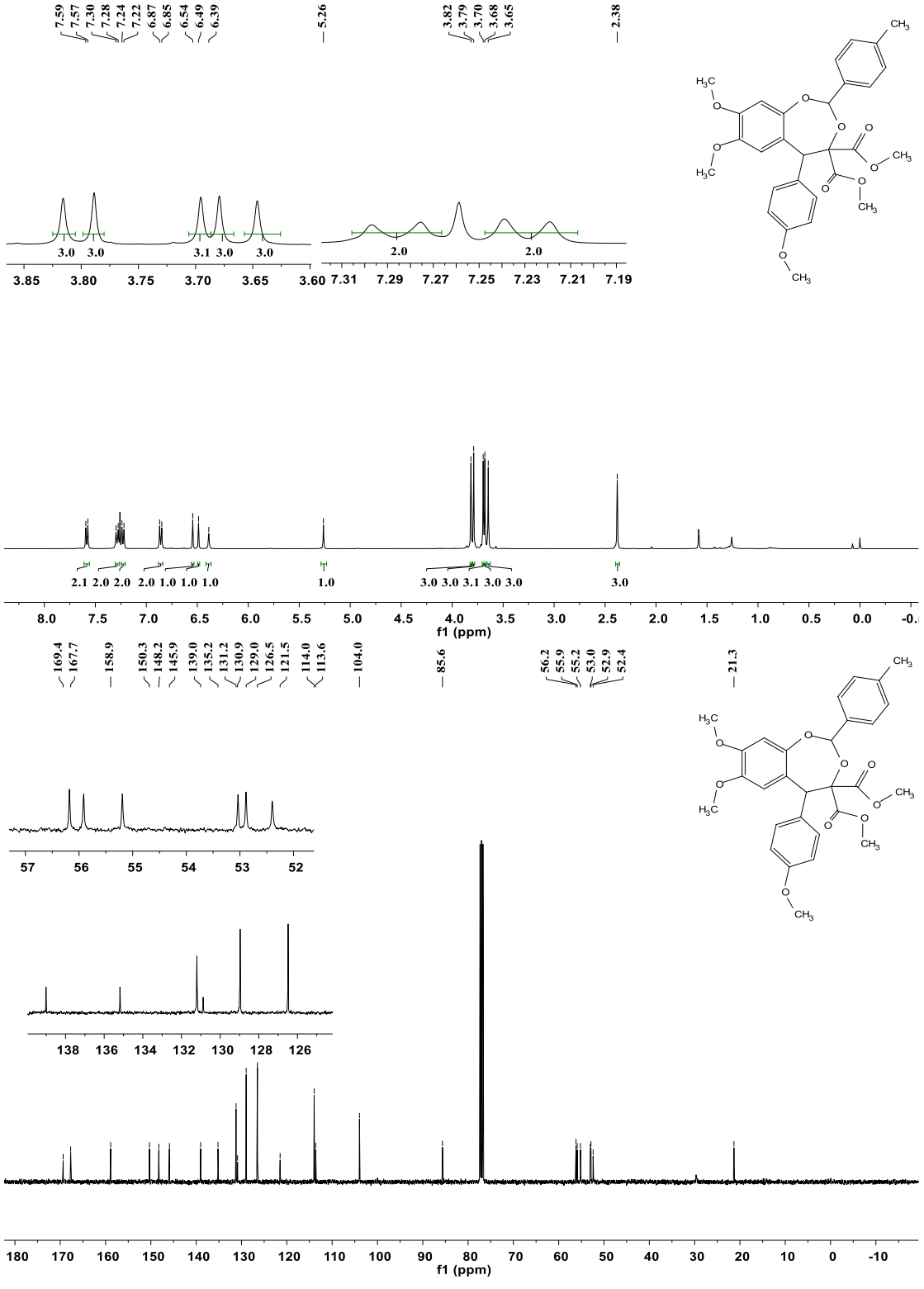
((*2S,5S*)-9-(4-methoxyphenyl)-6-(thiophen-3-yl)-8,9-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8-diyl)bis(phenylmethanone) (3ax)



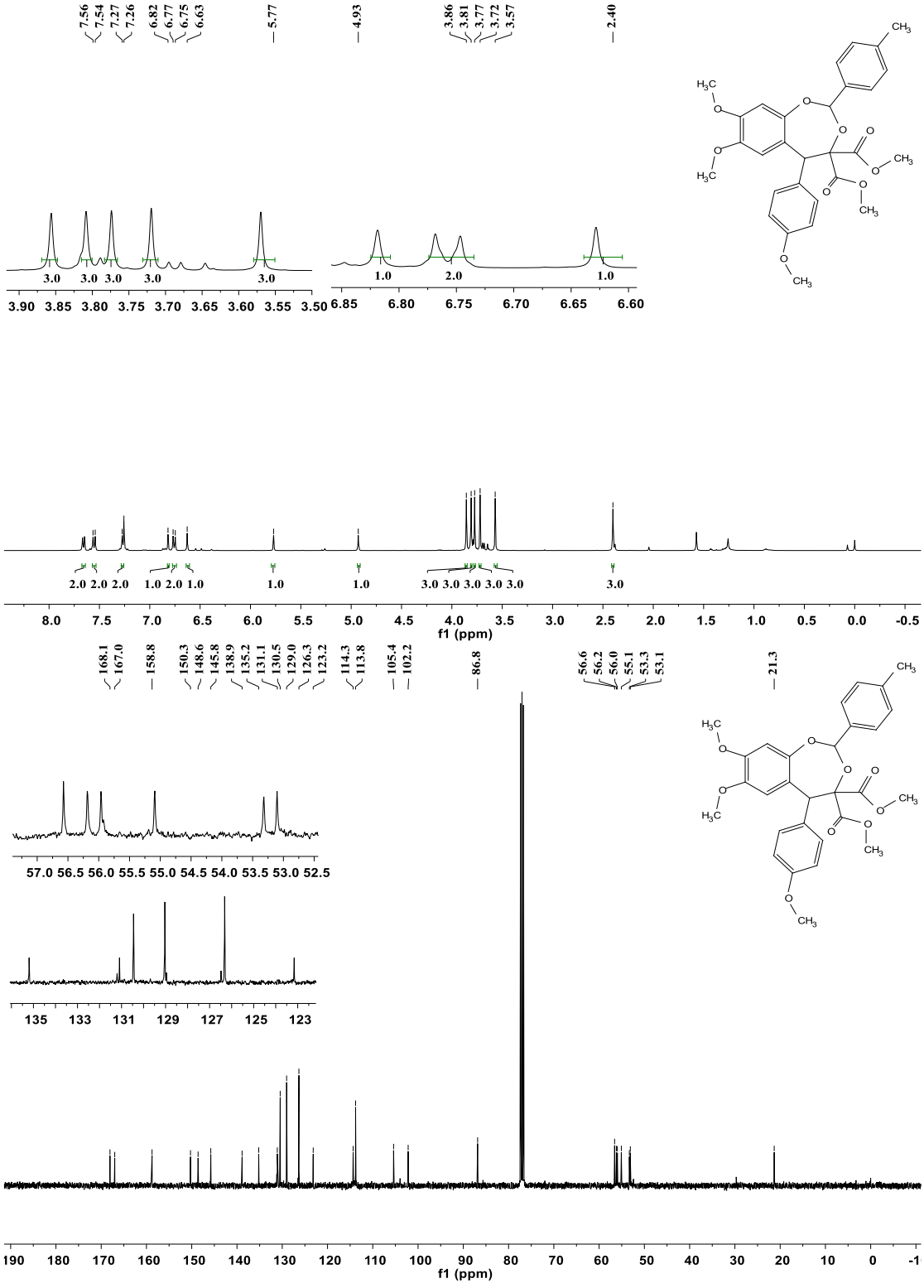
Dimethyl (*2S,5S*)-9-(4-ethoxyphenyl)-6-(p-tolyl)-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8,8(9H)-dicarboxylate (3ba):



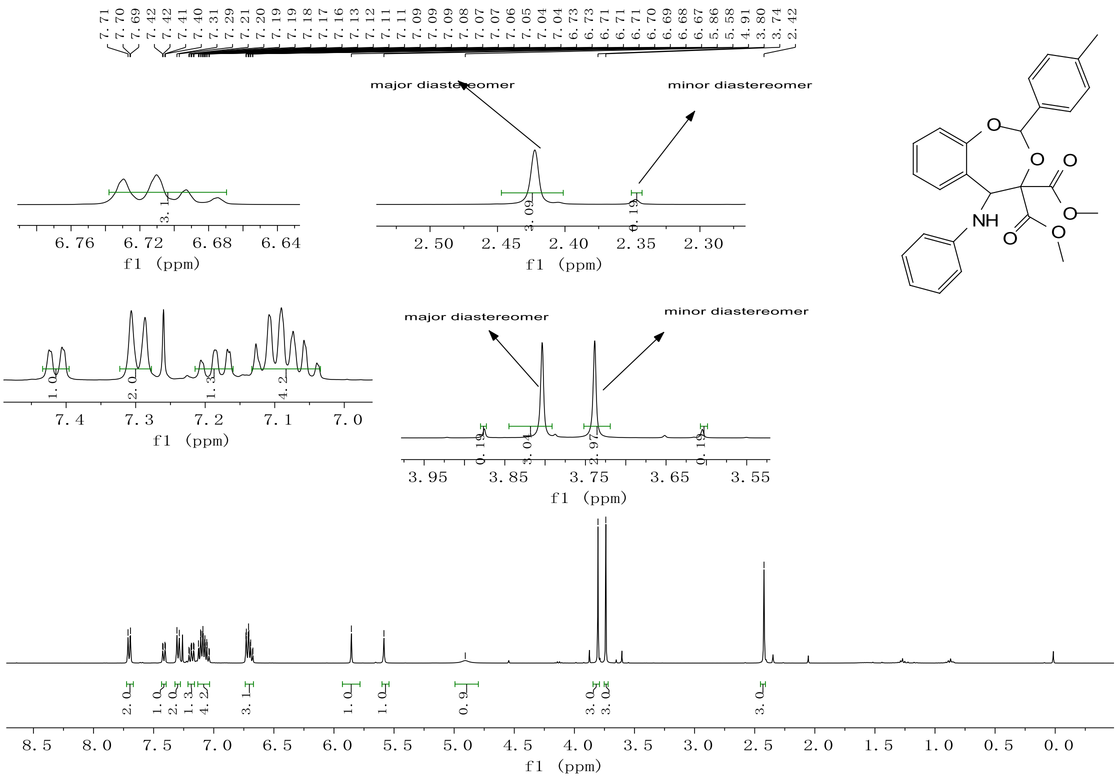
Dimethyl -5-(4-ethylphenyl)-7,8-dimethoxy-2-(p-tolyl)benzo[d][1,3]dioxepine-4,4(5H)-dicarboxylate (5a-major diastereomer):

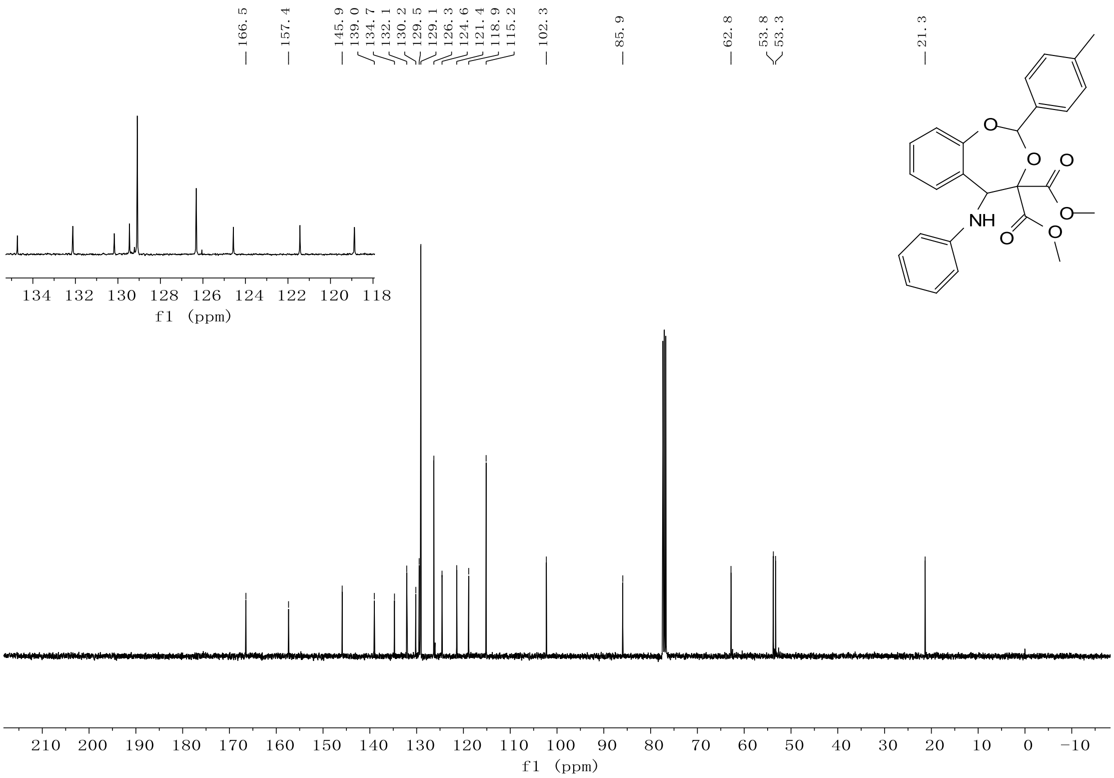


Dimethyl -5-(4-ethylphenyl)-7,8-dimethoxy-2-(p-tolyl)benzo[d][1,3]dioxepine-4,4(5H)-dicarboxylate (5a-minor diastereomer):

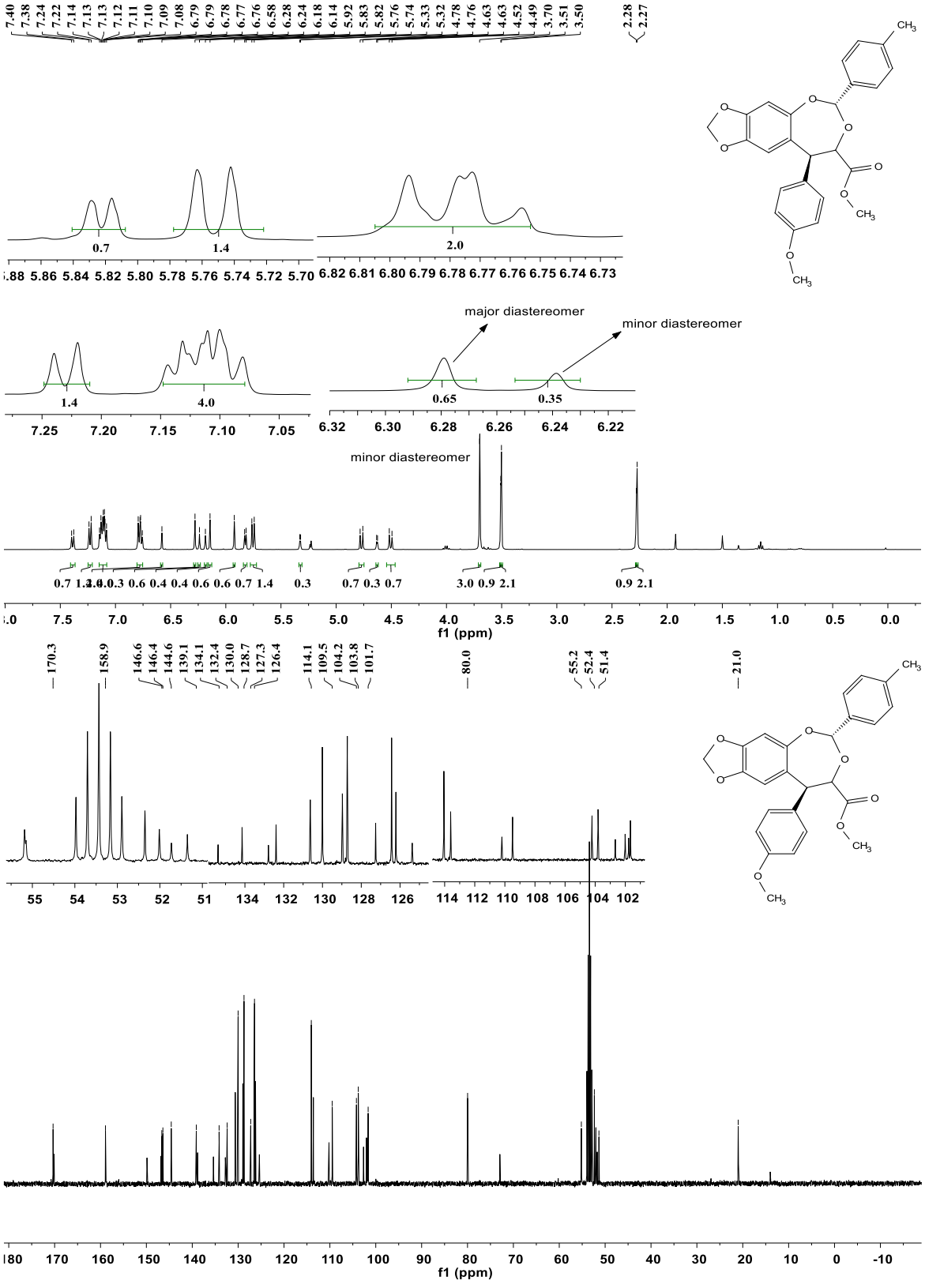


Dimethyl 5-(phenylamino)-2-(p-tolyl)benzo[d][1,3]dioxepine-4,4(5H)-dicarboxylate (3da):

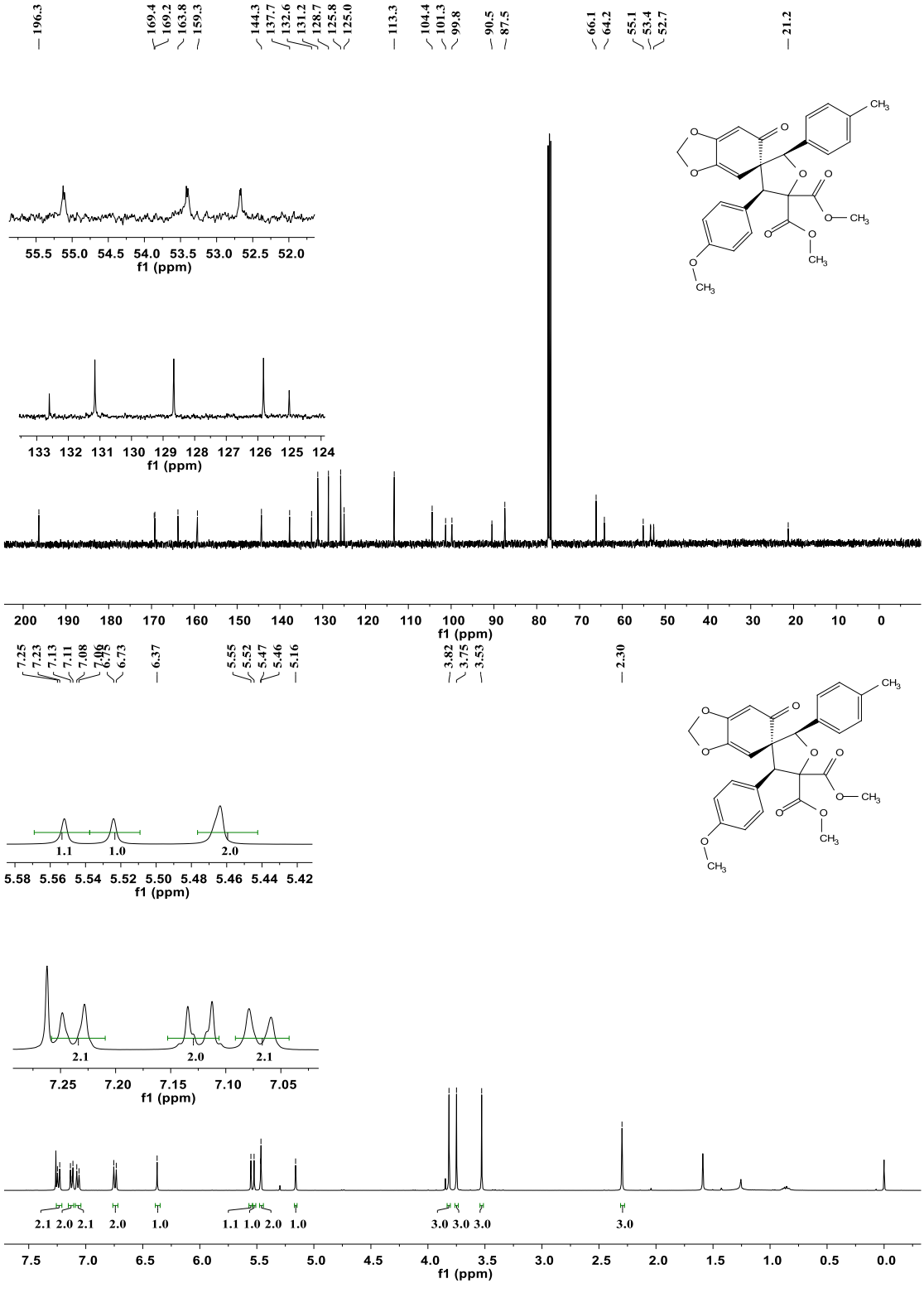




Methyl (2*S*, 6*S*)-9-(4-methoxyphenyl)-6-(p-tolyl)-8,9-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]dioxepine-8-carboxylate (4a):



Dimethyl (1*R*,4*S*,5*S*)-4'-(4-methoxyphenyl)-6-oxo-2'-(p-tolyl)-2'H,6H-spiro[benzo[d][1,3]dioxole-5,3'-furan]-5',5'(4'H)-dicarboxylate (5a):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163.8
159.3
144.3
137.7
132.6
131.2
128.7
125.8
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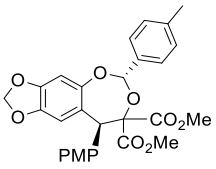
104.4
101.3
99.8
90.5
87.5
66.1
64.2
55.1
53.4
52.7
21.2
55.5 55.0 54.5 54.0 53.5 53.0 52.5 52.0
f1 (ppm)
133 132 131 130 129 128 127 126 125 124
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
7.25
7.23
7.13
7.11
7.08
7.06
6.73
6.37
5.55
5.52
5.47
5.46
5.16
3.82
3.75
3.53
2.30
1.1
1.0
2.0
5.58 5.56 5.54 5.52 5.50 5.48 5.46 5.44 5.42
f1 (ppm)
2.1
2.0
2.1
7.25 7.20 7.15 7.10 7.05
f1 (ppm)
2.1 2.0 2.1
2.0
1.0
1.1 1.0 2.0 1.0
3.0 3.0 3.0
3.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

15 Copies of CD Spectra for Products



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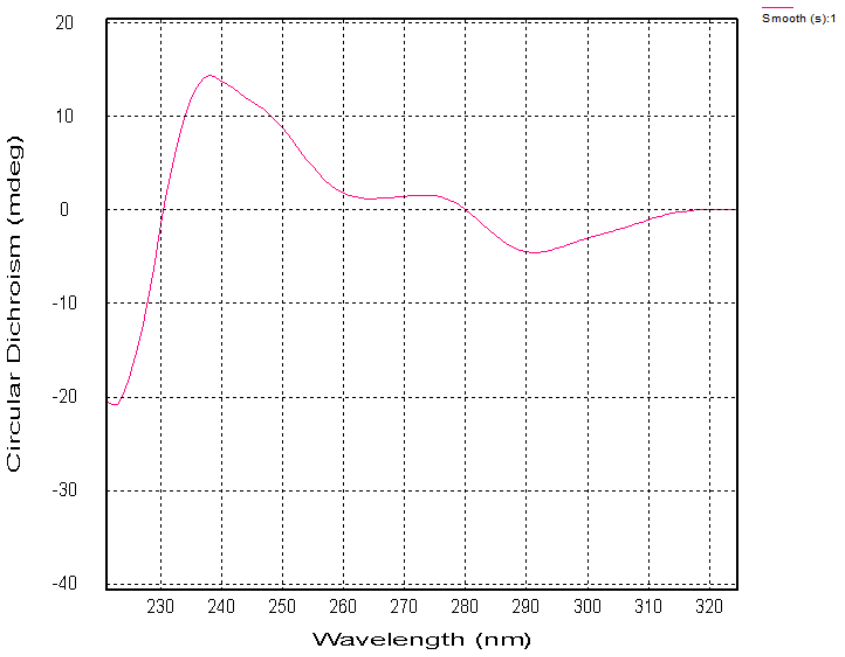

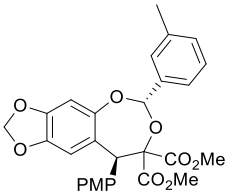

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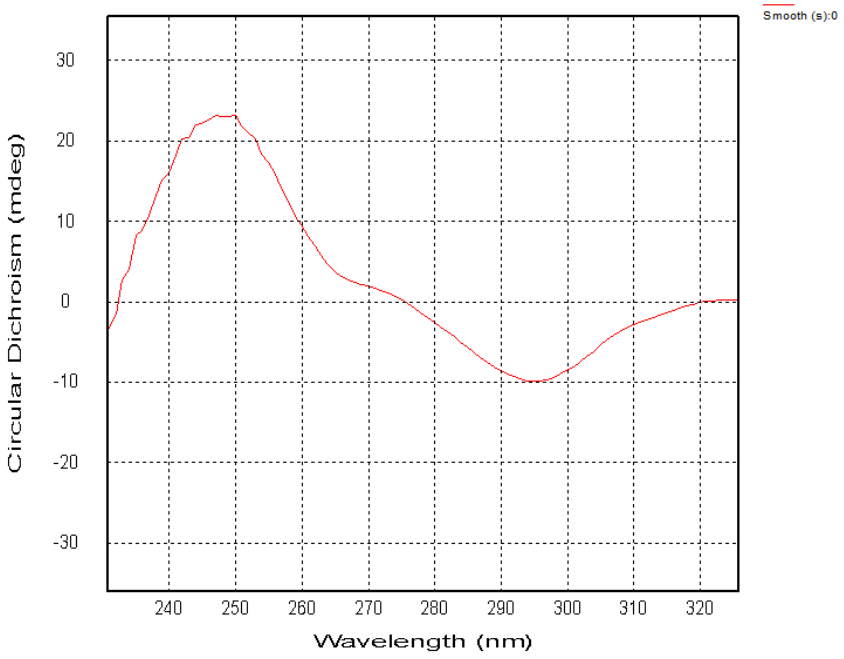
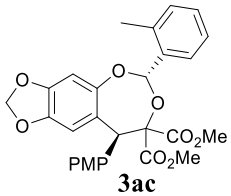
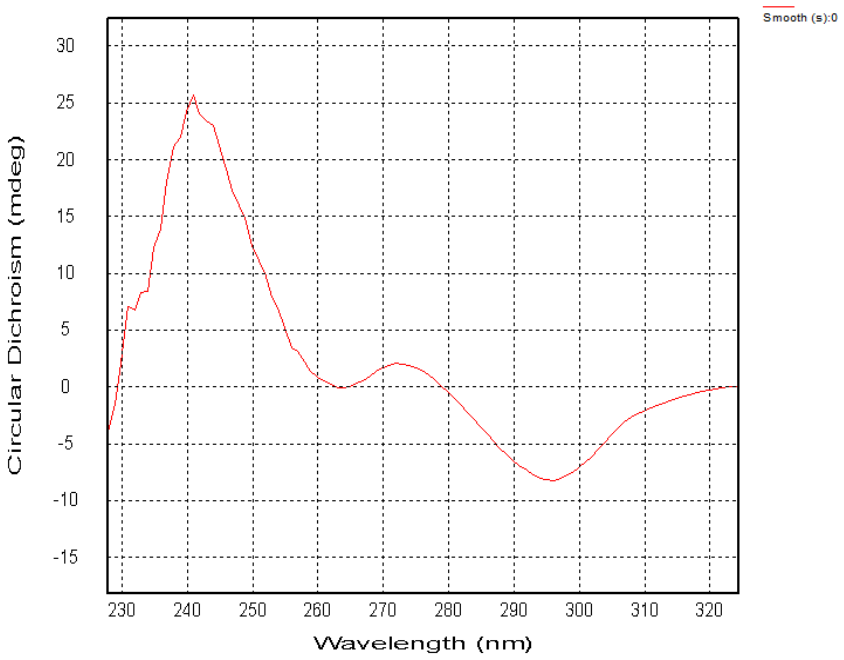



O
O
O
O
CO2Me
CO2Me
PMP

3ac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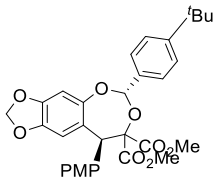
300
310
320
Wavelength (nm)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O
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O
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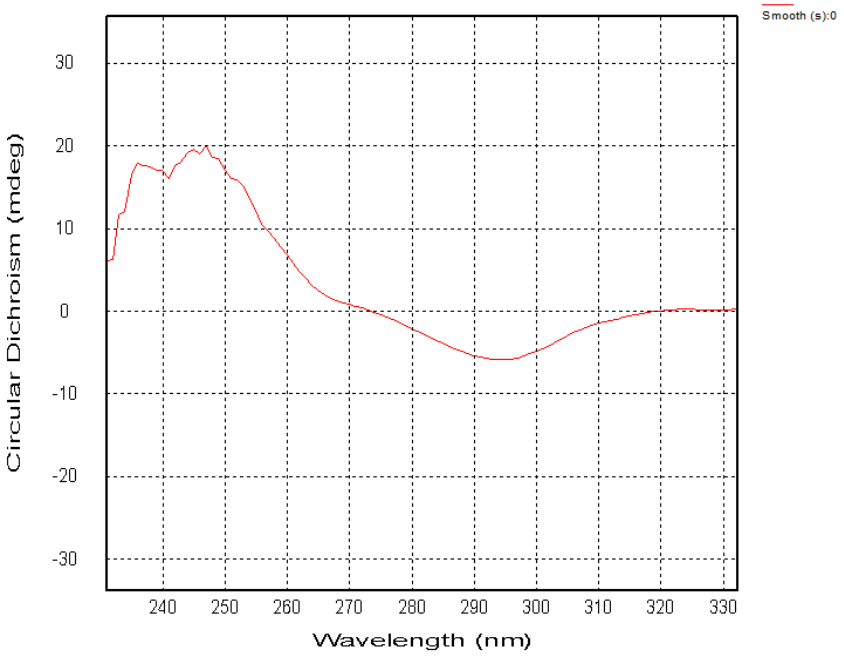
CO2Me
PMP

3ad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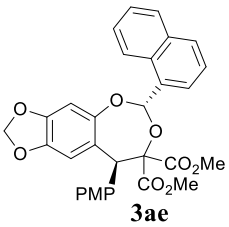
Wavelength (nm)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CO2Me

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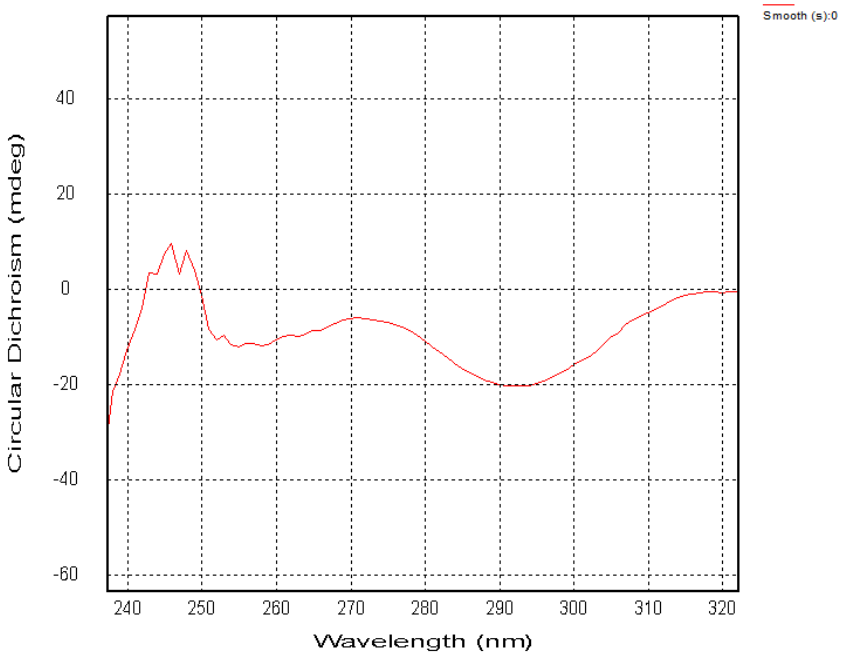
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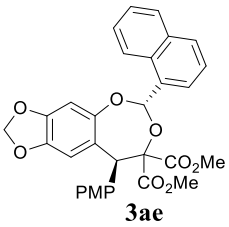
Wavelength (nm)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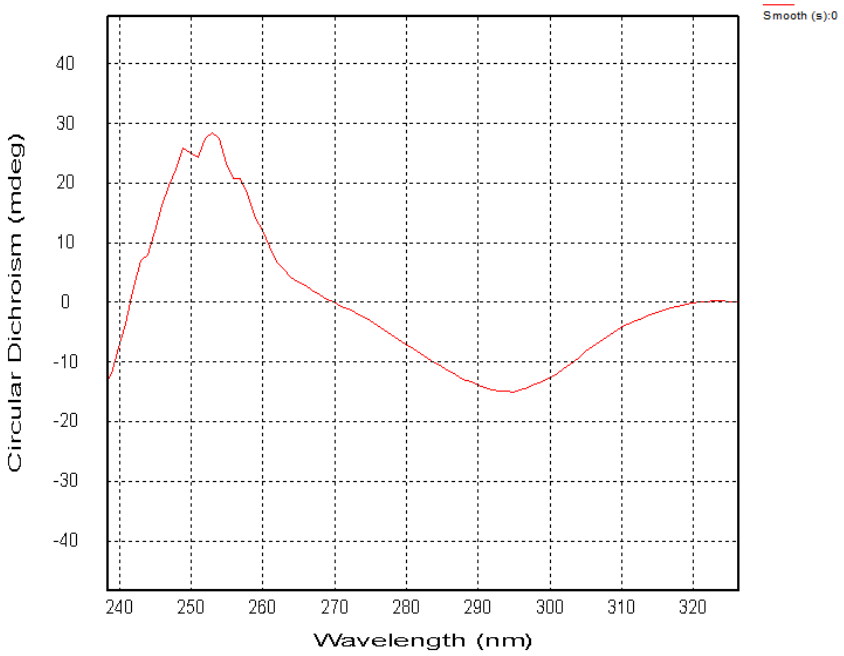
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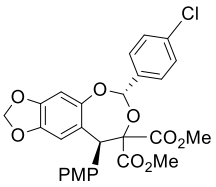
Wavelength (nm)


Cl
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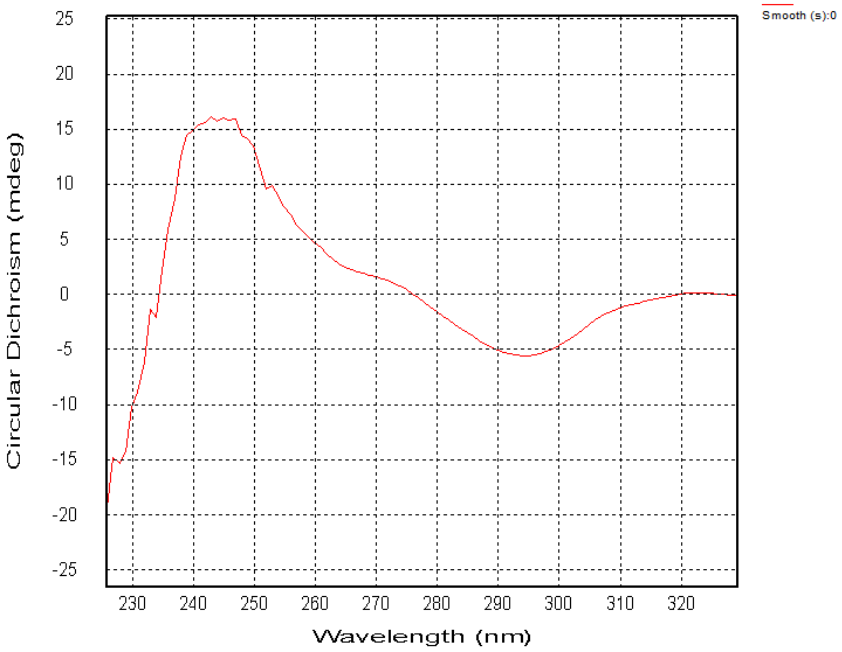
O
O
CO2Me
CO2Me
PMP

3ag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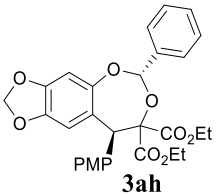
Wavelength (nm)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O
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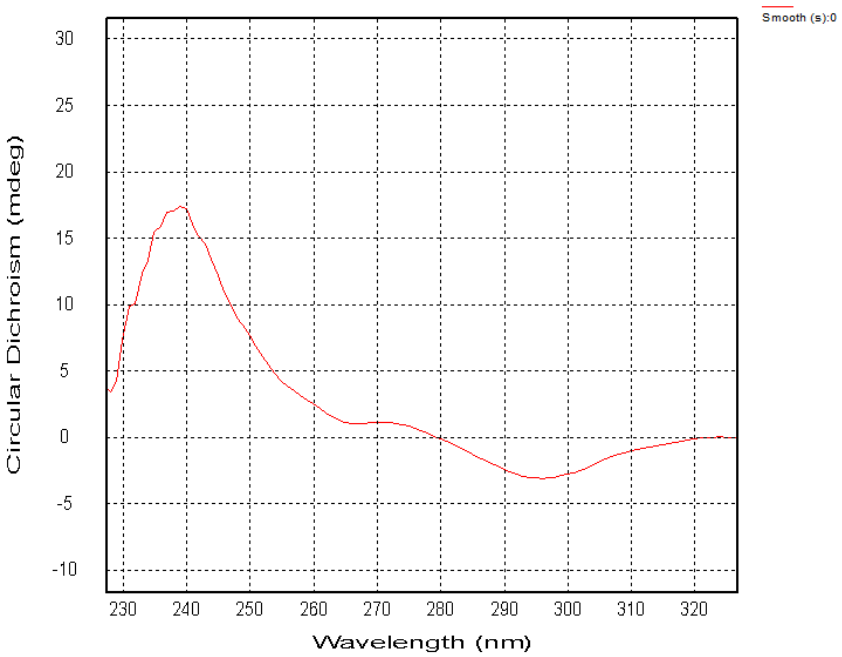
O
CO2Et
CO2Et
PMP

3ah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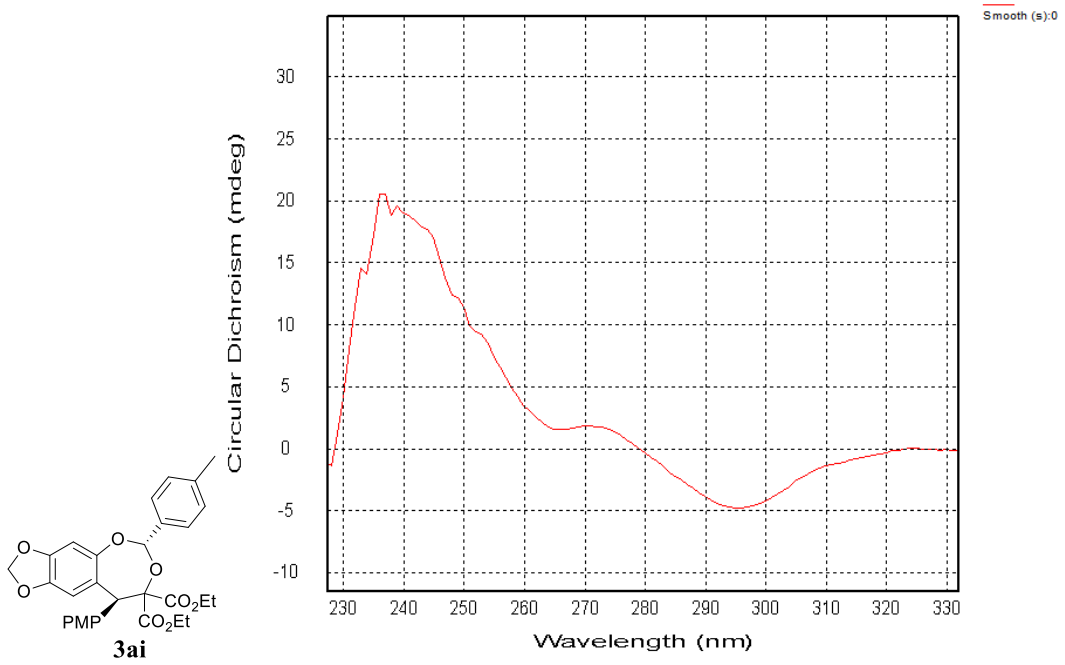
Wavelength (nm)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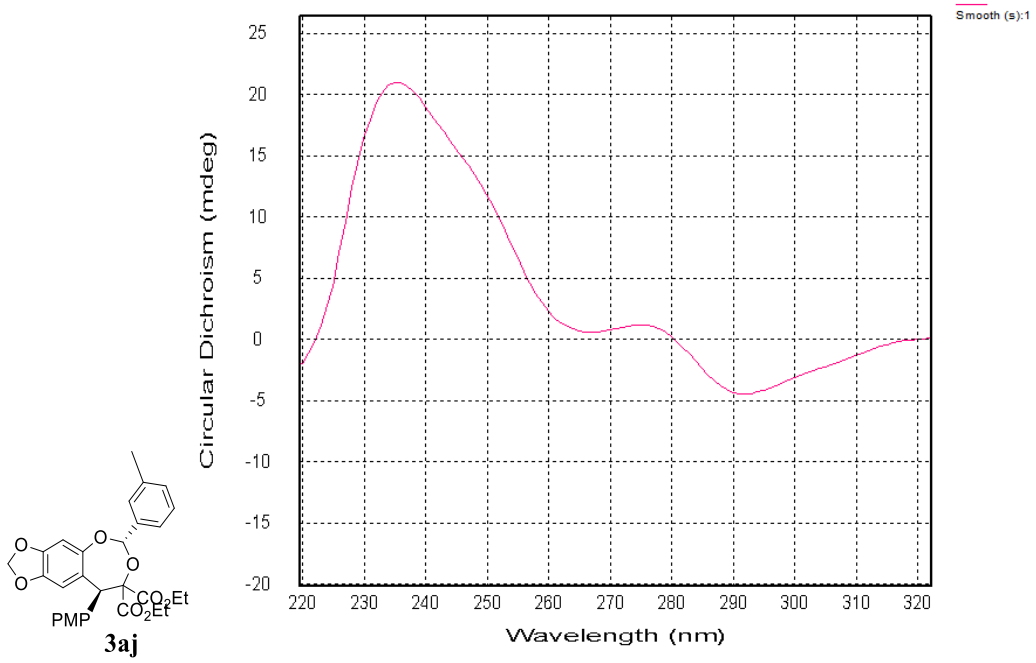
Wavelength (nm)
PMP
CO2Et
CO2Et

3ai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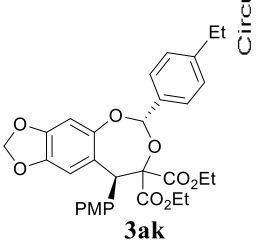
Wavelength (nm)
PMP
CO2Et
CO2Et

3aj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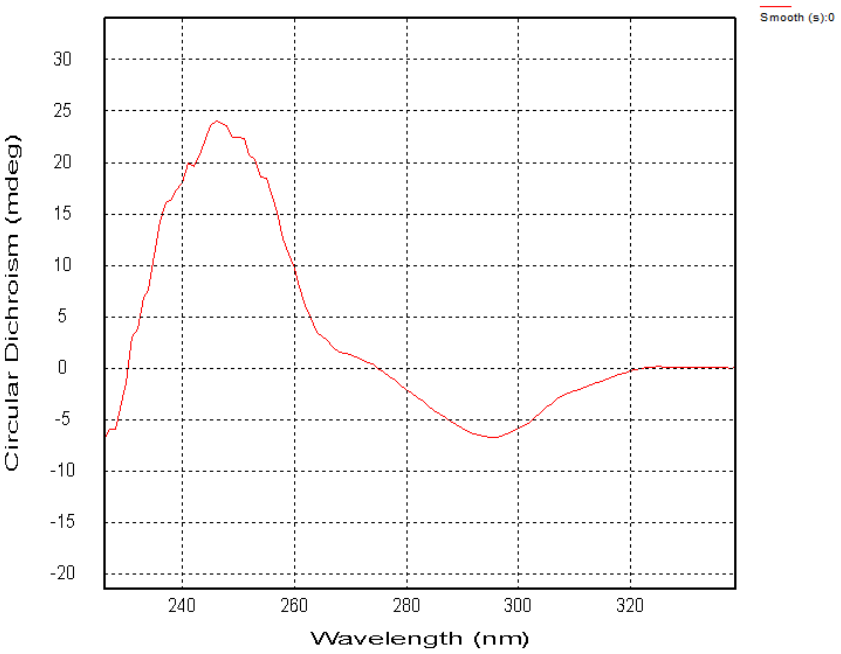
O
O
CO2Et
CO2Et
PMP

3ak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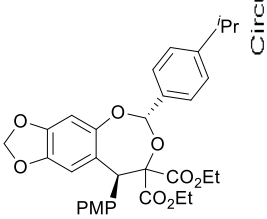
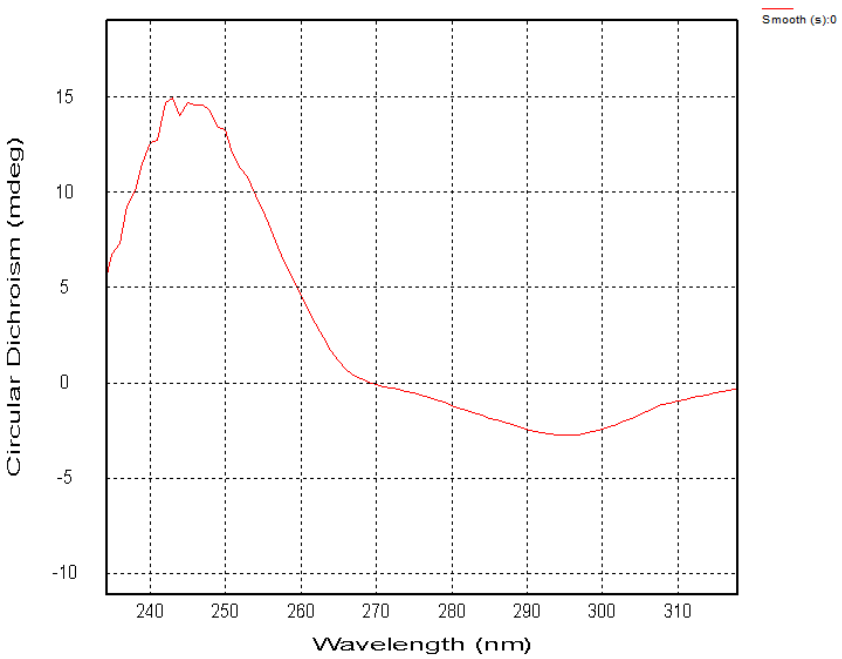
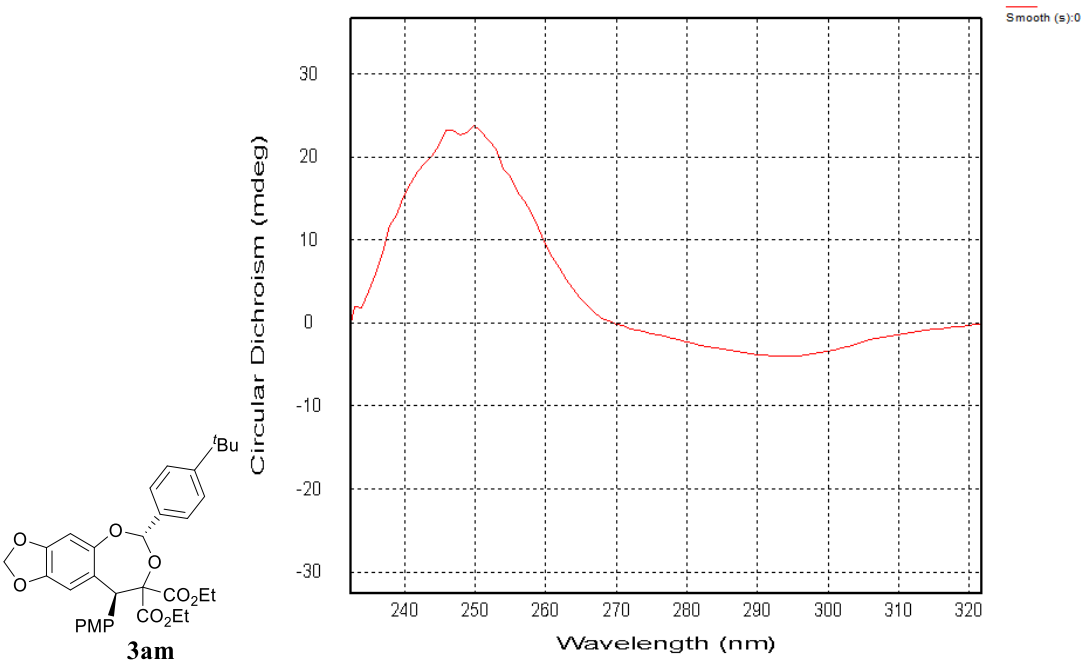
0
-5
-10
-15
-20
240
260
280
300
320
Wavelength (nm)

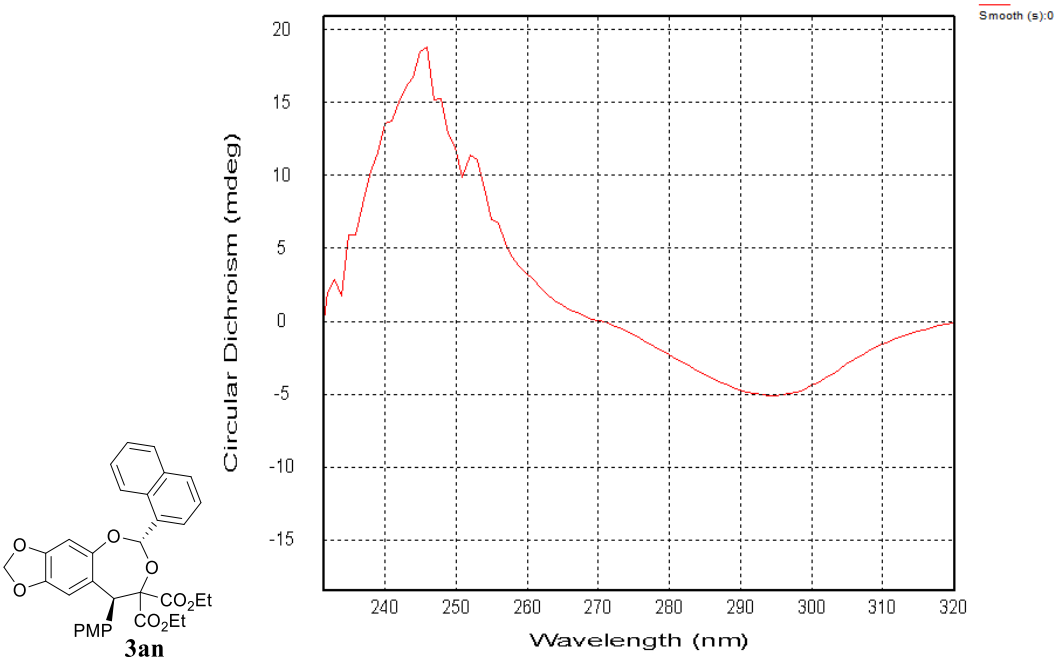

iPr
O
O
O
O
CO2Et
CO2Et
PMP

3al


Smooth (s):0
Circular Dichroism (mdeg)
15
10
5
0
-5
-10
240
250
260
270
280
290
300
310
Wavelength (nm)


Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
240
250
260
270
280
290
300
310
320
Wavelength (nm)
tBu
O
O
O
O
CO2Et
CO2Et
PMP

3am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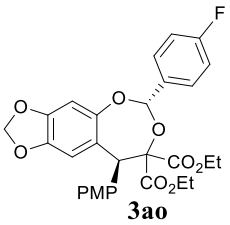
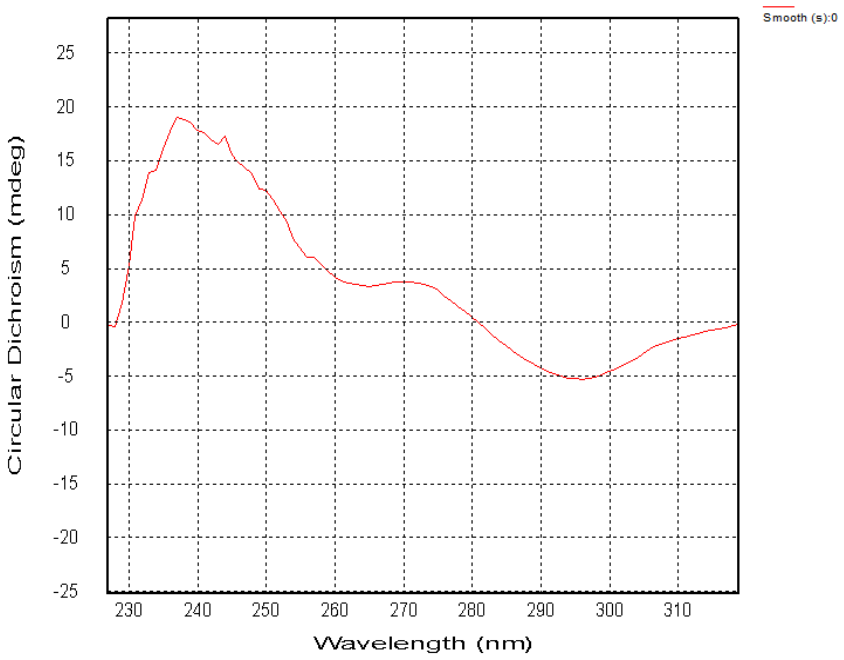
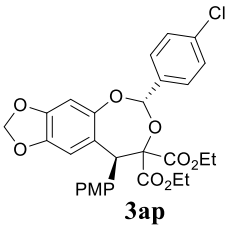
Circular Dichroism (mdeg)
20
15
10
5
0
-5
-10
-15
240
250
260
270
280
290
300
310
320
Wavelength (nm)
O
O
O
O
CO2Et
CO2Et
PMP

3an

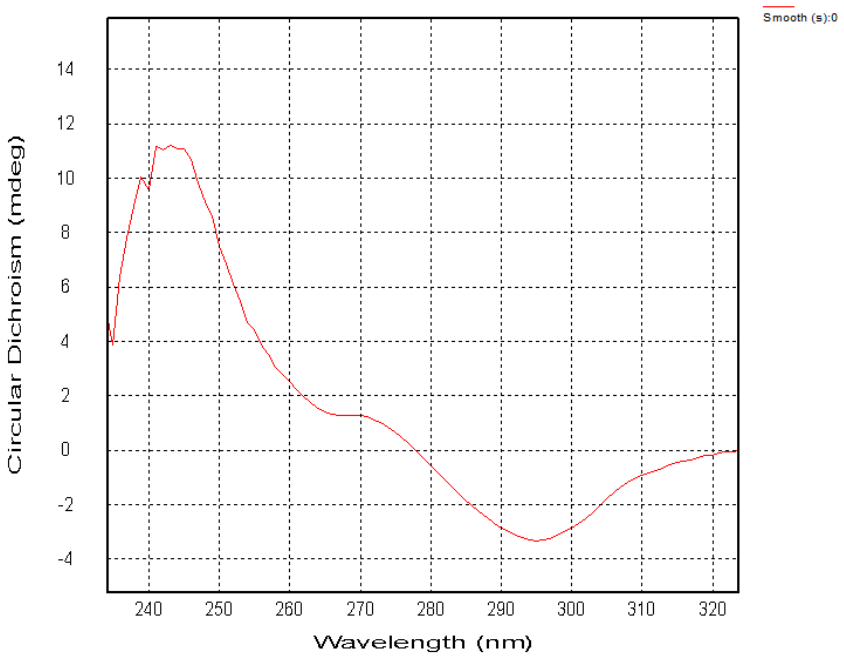

F
O
O
O
O
CO2Et
CO2Et
PMP

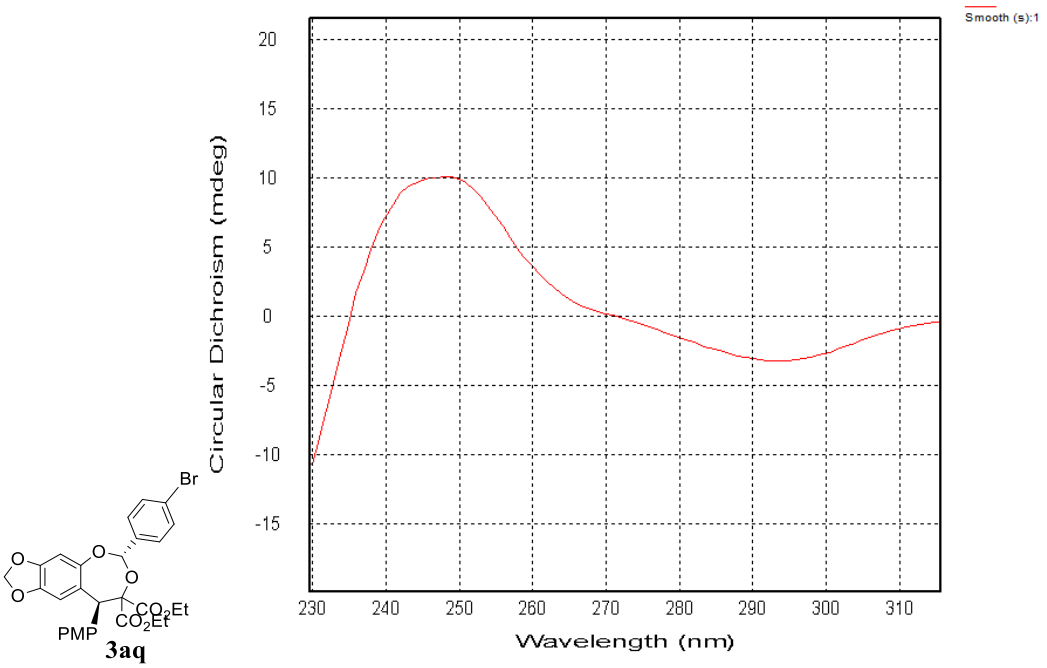
3ao


Smooth (s):0
Circular Dichroism (mdeg)
25
20
15
10
5
0
-5
-10
-15
-20
-25
230
240
250
260
270
280
290
300
310
Wavelength (nm)

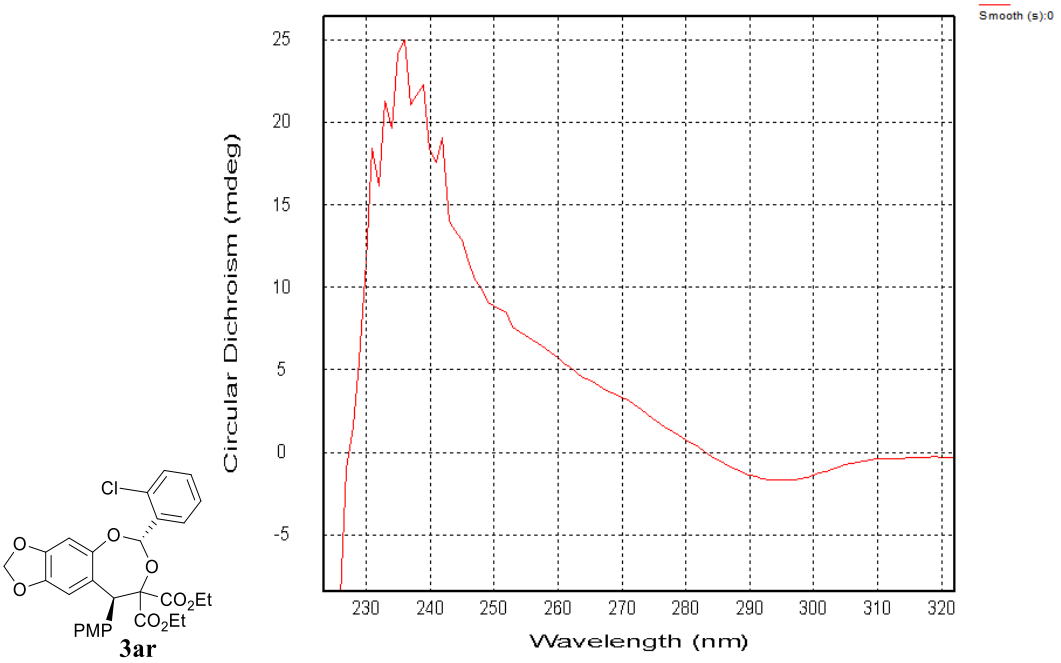

Cl
O
O
O
O
CO2Et
CO2Et
PMP

3ap


Smooth (s):0
Circular Dichroism (mdeg)
14
12
10
8
6
4
2
0
-2
-4
240
250
260
270
280
290
300
310
320
Wavelength (nm)


Smooth (s):1
Circular Dichroism (mdeg)
20
15
10
5
0
-5
-10
-15
230
240
250
260
270
280
290
300
310
Wavelength (nm)
Br
O
O
O
O
CO2Et
CO2Et
PMP

3aq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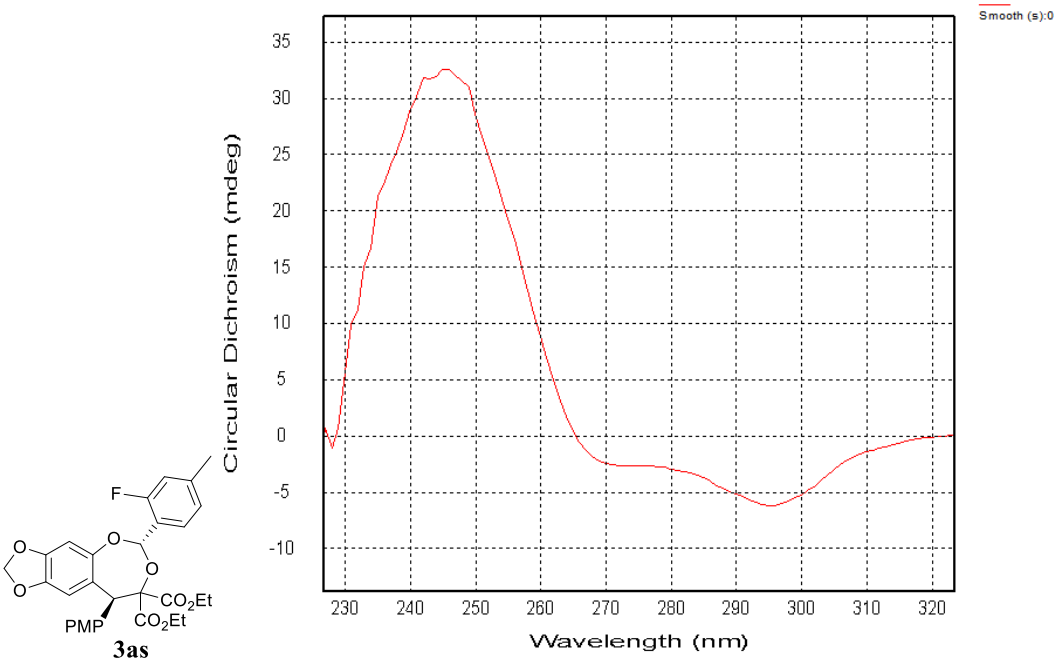
Circular Dichroism (mdeg)
25
20
15
10
5
0
-5
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
Cl
O
O
O
O
CO2Et
CO2Et
PMP

3ar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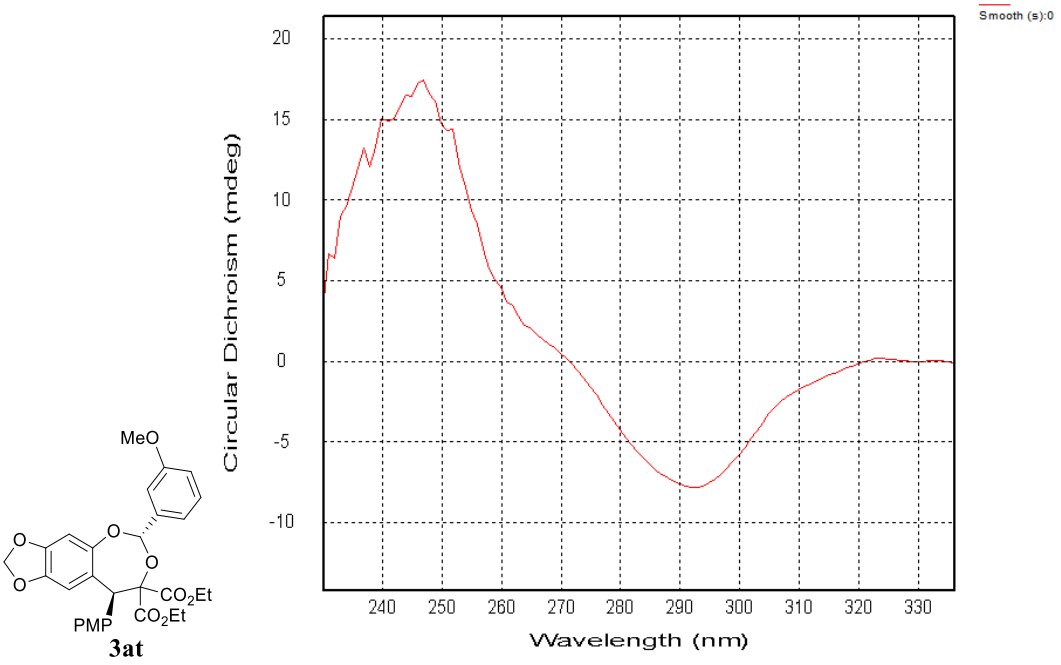
Circular Dichroism (mdeg)
35
30
25
20
15
10
5
0
-5
-10
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
F
O
O
O
O
CO2Et
CO2Et
PMP

3as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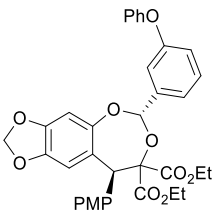
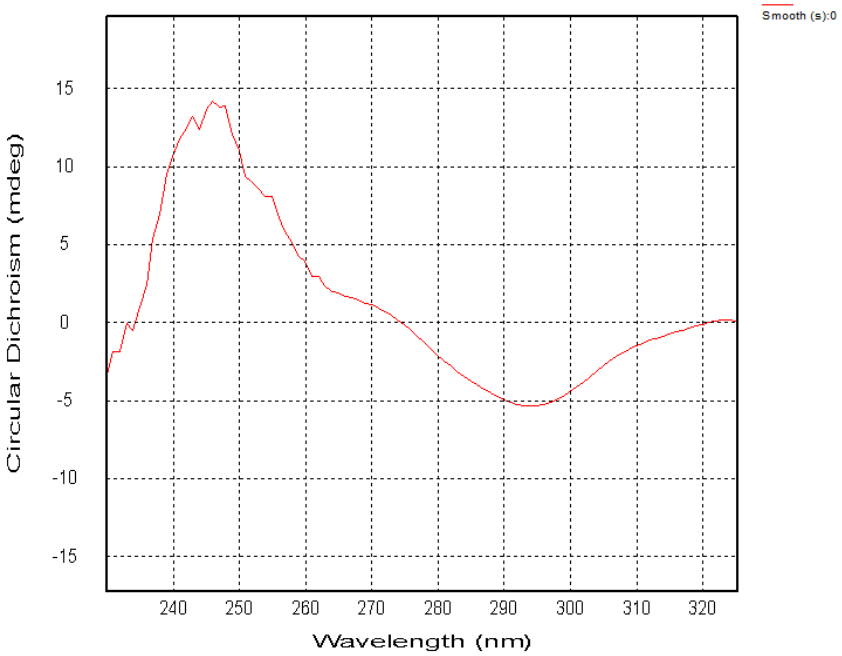
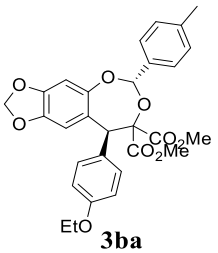
Circular Dichroism (mdeg)
20
15
10
5
0
-5
-10
240
250
260
270
280
290
300
310
320
330
Wavelength (nm)
MeO
O
O
O
O
CO2Et
CO2Et
PMP

3at

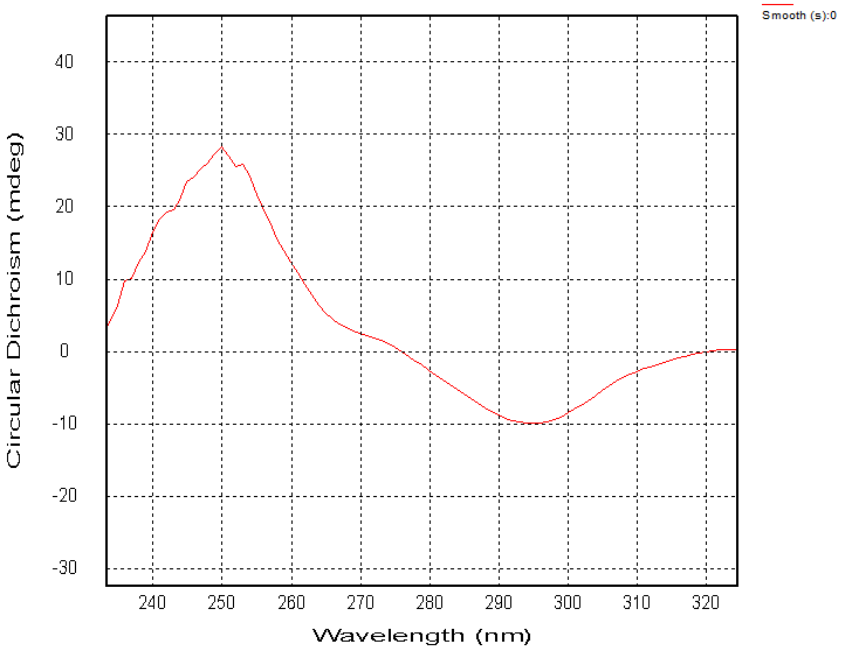

PhO
O
O
O
O
CO2Et
CO2Et
PMP

3au


Smooth (s):0
Circular Dichroism (mdeg)
15
10
5
0
-5
-10
-15
240
250
260
270
280
290
300
310
320
Wavelength (nm)


O
O
O
O
CO2Me
CO2Me
EtO

3ba


Smooth (s):0
Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
-30
240
250
260
270
280
290
300
310
320
Wavelength (nm)

16. Computational details

All calculations in this work including were carried out by using Gaussian 09 D.01 program package[1]. Geometries are optimized at the PBE0 level of density functional theory with consideration of the Grimme's dispersion correction[2, 3]. For the basis set, the central metal Sc, Y, Nd, Tb, Yb were calculated by the relativistic effective energy-consistent pseudopotential and its related basis sets ECP10MDF, ECP28MWB, ECP49MWB, ECP54MWB, ECP59MWB, respectively, while the rest of atoms including C, N, O, H were calculated by 6-31G(d,p) basis sets[4-15]. Frequency calculations on the same theoretical level were obtained to confirm local minimum structures and no imaginary frequency were observed.

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Cartesian coordinates of calculated structures

L_3-RaPr_2/Sc^{3+}

Sc	-0.07360000	0.06120000	0.22650000
O	-0.13410000	-1.26980000	-1.26290000
O	0.16260000	1.63560000	-0.96460000
O	1.97260000	0.26090000	0.37460000
O	0.52920000	-1.44370000	1.72740000
O	-2.11880000	-0.10370000	0.00660000
O	-0.91240000	1.22300000	1.90640000
N	1.18340000	1.91010000	-1.84030000
H	-0.52700000	1.54370000	2.73070000
H	-1.87610000	1.30880000	1.95290000
C	2.83830000	1.02760000	-0.12580000
N	-1.05360000	-1.35110000	-2.28210000
C	-2.87640000	-0.92610000	-0.57260000
N	4.10150000	0.91370000	0.21890000
C	4.53420000	-0.02710000	1.22520000
H	4.78850000	1.52040000	-0.21570000
C	1.34310000	0.79070000	-2.82840000
C	2.47580000	2.14420000	-1.08200000
C	0.93230000	3.28860000	-2.50670000
C	-1.16250000	-0.04020000	-3.01160000
C	-0.68600000	-2.53260000	-3.21670000
C	-2.39980000	-1.77960000	-1.72830000
N	-4.11310000	-1.08670000	-0.15530000
C	-4.60370000	-0.37050000	0.99990000
H	-4.72270000	-1.73870000	-0.63670000
C	5.17130000	-1.19930000	0.78910000
C	4.28550000	0.27160000	2.57310000
C	5.55960000	-2.11020000	1.77110000
C	5.37910000	-1.48350000	-0.68640000
C	5.31450000	-1.85760000	3.11700000
H	6.07040000	-3.02260000	1.48370000
C	4.68720000	-0.68230000	3.51180000
H	5.63390000	-2.57570000	3.86590000
H	4.53330000	-0.48820000	4.56910000
C	3.65200000	1.56950000	3.03680000
C	4.14310000	-2.18580000	-1.26590000
C	6.64270000	-2.29020000	-0.97770000
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H	6.56170000	-3.31910000	-0.61490000
H	7.52500000	-1.83530000	-0.52050000
H	6.81090000	-2.34380000	-2.05660000
H	3.22180000	-1.61870000	-1.08510000
H	4.01580000	-3.16950000	-0.80190000
H	4.25760000	-2.33800000	-2.34410000
C	2.31610000	1.32020000	3.74500000
C	4.60640000	2.36110000	3.93580000
H	3.44710000	2.19210000	2.15720000
H	4.82350000	1.81960000	4.86080000

H	4.16480000	3.32300000	4.21180000
H	5.55810000	2.55300000	3.43390000
H	1.62990000	0.75330000	3.10270000
H	1.85000000	2.27180000	4.02380000
H	2.45520000	0.74640000	4.66610000
C	2.24260000	3.50720000	-0.44670000
H	3.25480000	2.22840000	-1.84950000
C	1.67270000	4.32090000	-1.61510000
H	3.16560000	3.93200000	-0.04650000
H	1.51870000	3.41550000	0.36880000
C	0.61100000	5.35620000	-1.21780000
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C	-0.53550000	3.70920000	-2.52370000
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H	2.15460000	1.09030000	-3.49760000
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H	-1.54620000	0.68000000	-2.28910000
H	-1.91520000	-0.19100000	-3.79080000
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C	-1.45100000	-3.76140000	-2.65890000
H	-1.04170000	-2.22280000	-4.20220000
C	0.90800000	-4.03380000	-2.17320000
H	1.46170000	-2.06440000	-3.00430000
H	1.03300000	-3.28680000	-4.19770000
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H	1.80600000	-4.63850000	-2.31800000
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H	-0.64340000	-5.47790000	-1.55360000
H	-0.27750000	-5.47110000	-3.27280000
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H	-1.54620000	-3.34320000	-0.51600000
H	-3.10860000	-1.68910000	-2.56070000
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C	-5.40270000	0.99980000	3.24190000
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H	-6.30200000	2.73060000	-1.80020000
H	0.02940000	-1.98350000	2.35150000
H	1.47400000	-1.53100000	1.91900000

L_3-RaPr$_2$/Y^{3+}

Y	-0.08230000	0.05990000	0.50700000
O	0.39200000	1.71980000	-0.93590000
O	-0.38010000	-1.28170000	-1.23410000
O	2.19060000	0.12060000	0.25310000
O	0.82730000	0.71550000	2.70860000
O	-2.27290000	0.27910000	-0.18130000
O	-1.51710000	-0.69750000	2.28010000
O	1.01380000	-1.91980000	1.34270000
O	-0.93520000	2.21790000	1.29040000
N	1.38510000	1.81840000	-1.87370000
C	3.07640000	0.81440000	-0.28890000
N	-1.24840000	-1.21400000	-2.29420000
C	-3.05610000	-0.56670000	-0.66180000
C	1.40400000	0.63000000	-2.79090000
C	2.74000000	1.96890000	-1.20570000
C	1.27170000	3.17250000	-2.59790000
N	4.35680000	0.57090000	-0.05720000
C	4.74930000	-0.45400000	0.87790000
C	-1.16140000	0.10970000	-3.00450000
C	-2.66850000	-1.45820000	-1.82130000
C	-1.00710000	-2.40970000	-3.24980000
N	-4.27300000	-0.72590000	-0.15840000
C	-4.63970000	-0.05340000	1.05990000
C	0.17370000	0.42500000	-3.65830000
C	-0.15210000	3.65800000	-2.87020000
C	1.91940000	4.17870000	-1.61240000
C	-0.16520000	5.10380000	-2.34890000

C	0.76620000	5.06650000	-1.13960000
C	2.65520000	3.34440000	-0.55320000
C	4.61780000	-1.79840000	0.48490000
C	5.20360000	-0.05490000	2.14100000
C	5.49610000	-1.06670000	3.06060000
C	5.35350000	1.41100000	2.50500000
C	5.33200000	-2.40370000	2.72470000
C	4.90600000	-2.76650000	1.44890000
C	4.29450000	-2.17430000	-0.95020000
C	6.47880000	1.67460000	3.50350000
C	4.02730000	1.97470000	3.02960000
C	3.70770000	-3.57430000	-1.10280000
C	5.55130000	-2.02470000	-1.81700000
C	0.39560000	-3.00630000	-3.14970000
C	-1.98830000	-3.52100000	-2.79470000
C	0.25330000	-4.18630000	-2.18630000
C	-1.11870000	-4.75790000	-2.53690000
C	-2.67990000	-2.95430000	-1.55120000
C	-4.64560000	-0.82490000	2.24160000
C	-4.90260000	1.32160000	1.03240000
C	-4.86740000	-0.14450000	3.44210000
C	-4.50420000	-2.33770000	2.18540000
C	-5.08170000	1.23280000	3.45400000
C	-5.11360000	1.95030000	2.26560000
C	-5.03020000	2.11140000	-0.25610000
C	-4.03770000	-2.96750000	3.49500000
C	-5.83530000	-2.96510000	1.74700000
C	-3.97570000	3.21480000	-0.37590000
C	-6.44320000	2.69140000	-0.38400000
H	5.06490000	1.13000000	-0.51770000
H	-4.88960000	-1.42890000	-0.54710000
H	1.57350000	-0.23680000	-2.15160000
H	2.27050000	0.76520000	-3.44510000
H	0.43960000	-0.36740000	-4.36640000
H	0.00390000	1.31090000	-4.27880000
H	-1.43060000	0.86340000	-2.26710000
H	-1.92840000	0.08420000	-3.78400000
H	1.86350000	3.05000000	-3.50970000
H	-0.42370000	3.58750000	-3.92600000
H	-0.85210000	3.05240000	-2.28860000
H	-1.17340000	5.45110000	-2.11040000
H	0.23630000	5.78340000	-3.10780000
H	0.26190000	4.59910000	-0.28270000
H	1.09810000	6.05630000	-0.81850000
H	2.63670000	4.78910000	-2.16950000
H	3.65040000	3.72670000	-0.31720000
H	2.08600000	3.28650000	0.37850000
H	3.46800000	2.00190000	-2.02470000
H	5.86780000	-0.80660000	4.04570000
H	4.83580000	-3.81850000	1.19430000
H	5.60270000	1.96280000	1.58850000
H	7.41900000	1.22300000	3.17740000

H	6.24100000	1.28890000	4.49940000
H	6.63950000	2.75080000	3.60740000
H	4.12870000	3.03250000	3.29020000
H	3.72720000	1.44120000	3.94030000
H	3.22930000	1.89010000	2.28110000
H	3.54010000	-1.47030000	-1.32750000
H	5.96290000	-1.01160000	-1.77350000
H	5.33200000	-2.25830000	-2.86330000
H	6.33390000	-2.70900000	-1.47710000
H	2.82280000	-3.72180000	-0.47410000
H	4.43450000	-4.35240000	-0.85360000
H	3.41390000	-3.74000000	-2.14290000
H	-1.24180000	-2.02750000	-4.24590000
H	1.15470000	-2.28480000	-2.84510000
H	0.66060000	-3.37150000	-4.14840000
H	1.05590000	-4.91890000	-2.29460000
H	0.26930000	-3.81490000	-1.15570000
H	-1.53850000	-5.40370000	-1.76050000
H	-1.05280000	-5.35800000	-3.44970000
H	-2.74020000	-3.70480000	-3.56760000
H	-3.69170000	-3.34630000	-1.42400000
H	-2.10820000	-3.16650000	-0.64210000
H	-3.32090000	-1.23690000	-2.67600000
H	-4.89410000	-0.69620000	4.37570000
H	-5.33410000	3.01350000	2.29080000
H	-3.74860000	-2.57540000	1.42190000
H	-6.20050000	-2.57350000	0.79040000
H	-6.61310000	-2.75980000	2.48800000
H	-5.73800000	-4.05010000	1.65180000
H	-3.10590000	-2.52370000	3.86150000
H	-3.86360000	-4.03670000	3.34980000
H	-4.79080000	-2.87460000	4.28250000
H	-4.88460000	1.42080000	-1.09480000
H	-6.56390000	3.18410000	-1.35270000
H	-6.64370000	3.43590000	0.39220000
H	-7.20370000	1.91070000	-0.30150000
H	-2.96470000	2.79300000	-0.41380000
H	-4.03810000	3.92280000	0.45740000
H	-4.12990000	3.78660000	-1.29590000
H	-1.14110000	-0.67590000	3.16850000
H	-2.47760000	-0.55220000	2.36040000
H	1.97320000	-1.96240000	1.20990000
H	0.70700000	-2.78730000	1.62440000
H	0.60450000	1.61740000	2.97120000
H	1.74210000	0.55940000	2.97400000
H	-1.89570000	2.26830000	1.39630000
H	-0.71380000	2.80610000	0.55240000
H	-5.26040000	1.74040000	4.39690000
H	5.56790000	-3.17450000	3.45190000

L_3-RaPr_2/Nd^{3+}

Nd	-0.09990000	-0.10130000	-0.61070000
O	-0.46310000	1.21570000	1.29960000
O	0.53900000	-1.82540000	0.90050000
O	-0.86270000	-2.46050000	-1.23420000
O	2.28130000	-0.07350000	-0.25100000
O	-2.38000000	-0.35030000	0.18690000
O	1.13190000	1.92870000	-1.51400000
O	0.87370000	-0.95200000	-2.84080000
O	-1.69720000	0.43750000	-2.49660000
C	3.18890000	-0.72990000	0.29910000
N	-1.30230000	1.05800000	2.37130000
C	-2.74030000	1.28740000	1.94540000
C	-1.07870000	2.19650000	3.39920000
C	-1.14660000	-0.30340000	2.99250000
C	4.22880000	2.31000000	1.02140000
C	3.55870000	3.67260000	1.17080000
C	4.61000000	1.96950000	-0.40810000
C	5.46960000	2.22170000	1.91890000
H	3.50640000	1.56010000	1.37120000
N	-4.36960000	0.67830000	0.26670000
C	-3.14540000	0.46990000	0.73480000
C	-4.78200000	0.10960000	-0.98870000
H	-4.96470000	1.36310000	0.71660000
C	4.81900000	0.63910000	-0.81450000
C	4.87430000	2.96460000	-1.35180000
N	1.52810000	-1.86240000	1.84580000
N	4.46070000	-0.41770000	0.09810000
H	5.18780000	-0.94710000	0.56380000
C	5.31980000	0.28220000	-2.07270000
C	2.89910000	-1.91600000	1.19280000
C	1.44920000	-0.68420000	2.77230000
C	1.50370000	-3.22760000	2.55720000
C	5.58910000	1.32010000	-2.96950000
C	5.53210000	-1.17000000	-2.45840000
C	4.23290000	-1.77070000	-3.01000000
C	6.67980000	-1.37600000	-3.44440000
H	5.78800000	-1.72750000	-1.54730000
H	6.87930000	-2.44380000	-3.56570000
H	7.59900000	-0.89840000	-3.09620000
H	6.44300000	-0.97980000	-4.43640000
C	5.35370000	2.64260000	-2.61910000
H	5.99570000	1.09240000	-3.94870000
H	5.57080000	3.43470000	-3.32900000
H	4.74200000	4.00760000	-1.08510000
C	2.90310000	-3.28360000	0.51880000
H	3.61600000	-1.92090000	2.02230000
C	2.21780000	-4.17810000	1.56310000
H	3.92030000	-3.59940000	0.27890000
H	2.33120000	-3.24460000	-0.41220000
C	1.12570000	-5.13230000	1.07310000
H	2.97030000	-4.74830000	2.11640000
C	0.11440000	-3.80720000	2.82160000

H	2.08480000	-3.07550000	3.47140000
H	-0.54140000	-2.97050000	-0.47370000
C	0.19050000	-5.24220000	2.27530000
H	-0.15760000	-3.77510000	3.87930000
H	-0.62430000	-3.23310000	2.25580000
H	1.74470000	-0.78100000	-3.21890000
H	1.52270000	-6.09610000	0.74670000
H	0.60140000	-4.69170000	0.21430000
H	0.93530000	2.74910000	-1.97790000
C	0.20230000	-0.58780000	3.63590000
H	1.55520000	0.19870000	2.14160000
H	2.32050000	-0.75630000	3.43020000
H	0.07610000	-1.51310000	4.20640000
H	0.42170000	0.17610000	4.38940000
H	-1.91570000	-0.37390000	3.76740000
H	-1.37510000	-1.01950000	2.20520000
C	-2.79740000	2.79750000	1.77150000
H	-3.36590000	0.99310000	2.79810000
C	-2.09620000	3.30690000	3.03260000
H	-2.24950000	3.08160000	0.86720000
H	-3.82090000	3.17000000	1.68730000
C	-1.26450000	4.58110000	2.83660000
H	-2.83640000	3.42180000	3.82970000
C	0.30530000	2.83660000	3.31870000
C	0.11790000	4.07040000	2.43450000
H	0.57610000	3.14370000	4.33530000
H	1.07810000	2.15720000	2.95740000
H	-1.28870000	1.74450000	4.37150000
H	0.90100000	4.81740000	2.58100000
H	0.13130000	3.76790000	1.38200000
H	-1.71270000	5.25890000	2.10490000
H	-1.20240000	5.12830000	3.78240000
C	-4.76220000	0.96150000	-2.11410000
C	-5.12950000	-1.24390000	-1.05320000
C	-5.05910000	0.38600000	-3.35230000
C	-4.50530000	2.45130000	-1.96070000
C	-5.37200000	-0.96880000	-3.45430000
H	-5.06970000	1.00410000	-4.24360000
C	-5.41800000	-1.76590000	-2.31990000
H	-5.60940000	-1.39410000	-4.42450000
H	-5.70190000	-2.80990000	-2.41270000
C	-5.23820000	-2.12670000	0.17360000
C	-4.18360000	-3.23730000	0.16850000
C	-6.64860000	-2.71070000	0.30090000
H	-5.06040000	-1.50450000	1.05830000
H	-6.87590000	-3.39840000	-0.51890000
H	-7.40780000	-1.92460000	0.29740000
H	-6.74280000	-3.27110000	1.23510000
H	-4.28200000	-3.87550000	-0.71630000
H	-4.29980000	-3.88010000	1.04620000
H	-3.17440000	-2.81070000	0.19730000
C	-5.77430000	3.14910000	-1.45180000

C	-4.01220000	3.13110000	-3.23510000
H	-3.72040000	2.57780000	-1.19990000
H	-3.12500000	2.64060000	-3.64920000
H	-3.75190000	4.17120000	-3.02320000
H	-4.78300000	3.15080000	-4.01080000
H	-5.58900000	4.21340000	-1.28180000
H	-6.15560000	2.71940000	-0.51840000
H	-6.57740000	3.06060000	-2.18890000
H	3.93620000	-1.23700000	-3.92210000
H	3.42030000	-1.70920000	-2.27590000
H	4.37140000	-2.82280000	-3.27600000
H	5.93760000	1.23330000	1.87630000
H	5.21070000	2.43130000	2.96100000
H	6.22100000	2.95220000	1.60590000
H	2.68470000	3.77670000	0.51870000
H	4.24750000	4.49320000	0.95120000
H	3.22740000	3.80900000	2.20380000
H	-0.79340000	-5.64630000	2.02580000
H	0.62750000	-5.90850000	3.02640000
H	2.08390000	1.91470000	-1.32300000
H	0.62180000	-1.84660000	-3.10080000
H	-1.79780000	-2.67760000	-1.34520000
H	-2.67200000	0.40730000	-2.46970000
H	-1.44050000	0.44440000	-3.42570000

L_3-RaPr$_2$/Tb^{3+}

Tb	0.32310000	-0.36310000	0.71130000
O	-0.01180000	1.48680000	-0.65910000
O	-0.13680000	-1.86180000	-0.90910000
O	-2.01080000	-0.64260000	0.70660000
O	2.22340000	-0.02450000	-0.63480000
O	2.16370000	-1.90240000	1.36080000
O	-0.79380000	1.58630000	1.79610000
O	-0.24040000	-1.45380000	2.83980000
O	1.86530000	0.89430000	2.16320000
N	0.44250000	1.65020000	-1.94210000
C	2.71210000	1.04450000	-1.05360000
N	-1.17890000	-2.35770000	-1.62840000
C	-2.82280000	-1.27100000	-0.00880000
C	0.18920000	0.41850000	-2.77040000
C	1.91210000	2.01660000	-1.90220000
C	-0.18000000	2.90790000	-2.57160000
N	3.96350000	1.37470000	-0.75800000
C	4.69820000	0.61320000	0.21540000
C	-2.41120000	-2.52200000	-0.75610000
C	-1.39420000	-1.54930000	-2.88320000
C	-0.90430000	-3.82510000	-2.00730000
N	-4.10150000	-0.93480000	-0.07130000
C	-4.67570000	0.17360000	0.64130000
C	-1.26340000	-0.04480000	-2.69160000
C	-1.64470000	3.15590000	-2.21390000

C	0.64370000	4.07790000	-1.99600000
C	-1.67310000	4.61370000	-1.72550000
C	-0.31700000	4.80040000	-1.04750000
C	1.90830000	3.45830000	-1.38850000
C	5.07370000	-0.70600000	-0.07710000
C	4.94350000	1.23010000	1.46040000
C	5.52910000	0.44620000	2.45790000
C	5.85970000	-0.88560000	2.21860000
C	5.64840000	-1.44660000	0.96550000
C	0.53550000	-4.08560000	-2.44380000
C	-1.15640000	-4.59370000	-0.70070000
C	1.03570000	-5.17700000	-1.47920000
C	0.24730000	-4.93650000	-0.19230000
C	-2.02470000	-3.67440000	0.17470000
C	-4.74330000	0.13660000	2.04220000
C	-5.17890000	1.23900000	-0.12710000
C	-5.72940000	2.31850000	0.56200000
C	-5.77890000	2.32950000	1.95220000
C	-5.29730000	1.25010000	2.68010000
H	4.34120000	2.25650000	-1.08170000
H	-4.70710000	-1.45560000	-0.69430000
H	0.85110000	-0.34990000	-2.37560000
H	0.48490000	0.65510000	-3.79600000
H	-1.86360000	0.44000000	-3.46660000
H	-1.68820000	0.26180000	-1.73370000
H	-2.38230000	-1.81790000	-3.26490000
H	-0.65360000	-1.91810000	-3.59790000
H	-0.01600000	2.78470000	-3.64530000
H	-2.31270000	2.97410000	-3.05840000
H	-1.93590000	2.48820000	-1.39890000
H	-1.76260000	5.29710000	-2.57640000
H	-2.51830000	4.81530000	-1.06270000
H	-0.30970000	4.30930000	-0.06550000
H	-0.05200000	5.84870000	-0.89310000
H	0.90790000	4.74900000	-2.81890000
H	2.81830000	3.98400000	-1.68800000
H	1.85760000	3.46140000	-0.29600000
H	2.27150000	1.97820000	-2.93880000
H	5.74580000	0.88250000	3.42690000
H	6.31850000	-1.47600000	3.00550000
H	5.97060000	-2.46660000	0.77690000
H	-1.64490000	-4.05150000	-2.78040000
H	1.12230000	-3.17230000	-2.31080000
H	0.59800000	-4.38700000	-3.49140000
H	0.80070000	-6.16870000	-1.87920000
H	2.11870000	-5.13960000	-1.33790000
H	0.25480000	-5.79100000	0.48860000
H	0.65210000	-4.06460000	0.33650000
H	-1.69190000	-5.51810000	-0.93620000
H	-2.92210000	-4.16280000	0.56000000
H	-1.45820000	-3.29000000	1.02730000
H	-3.20840000	-2.83980000	-1.43590000

H	-6.13330000	3.15920000	0.00920000
H	-6.21750000	3.17700000	2.46940000
H	-5.38310000	1.25770000	3.76260000
H	2.15620000	-2.85650000	1.49500000
H	-0.78920000	2.19780000	1.04080000
C	-4.33090000	-1.06840000	2.86400000
C	-5.56090000	-1.74880000	3.47460000
C	-3.32250000	-0.69690000	3.95330000
H	-3.85120000	-1.79840000	2.20310000
H	-6.27230000	-2.04890000	2.70100000
H	-5.27030000	-2.64110000	4.03690000
H	-6.08330000	-1.07640000	4.16110000
H	-2.48150000	-0.12140000	3.54270000
H	-3.76970000	-0.07140000	4.73090000
H	-2.95330000	-1.59740000	4.46010000
C	-5.17730000	1.17620000	-1.64320000
C	-5.25780000	2.54630000	-2.31150000
C	-6.32950000	0.29190000	-2.14290000
H	-4.22790000	0.71150000	-1.95260000
H	-4.51460000	3.24220000	-1.91210000
H	-5.09770000	2.44850000	-3.38900000
H	-6.24530000	2.99880000	-2.18200000
H	-6.31880000	-0.72240000	-1.72510000
H	-7.29030000	0.73130000	-1.86060000
H	-6.30780000	0.20290000	-3.23280000
C	4.96680000	-1.31240000	-1.46350000
C	4.16370000	-2.61550000	-1.47830000
C	6.37080000	-1.52770000	-2.04080000
H	4.45190000	-0.59660000	-2.11280000
H	3.13900000	-2.46310000	-1.12210000
H	4.10790000	-3.00870000	-2.49760000
H	4.64090000	-3.38830000	-0.86640000
H	6.94580000	-0.59820000	-2.05190000
H	6.93330000	-2.26080000	-1.45500000
H	6.30580000	-1.90110000	-3.06660000
C	4.64960000	2.70700000	1.66850000
C	5.73790000	3.55620000	0.99540000
C	4.51120000	3.11330000	3.13420000
H	3.69160000	2.92720000	1.17420000
H	5.86640000	3.32900000	-0.06950000
H	5.50830000	4.62120000	1.08700000
H	6.70620000	3.37710000	1.47110000
H	3.78990000	2.49510000	3.68160000
H	5.46550000	3.04900000	3.66450000
H	4.18100000	4.15270000	3.20270000
H	-1.72640000	1.44900000	2.01380000
H	0.41310000	-1.59880000	3.53440000
H	-1.10600000	-1.38930000	3.26850000
H	3.02520000	-1.68490000	0.96630000
H	2.82830000	0.80400000	2.24680000
H	1.57050000	1.58600000	2.76620000

L_3-RaPr$_2$/Yb^{3+}

Yb	-0.29620000	0.29420000	0.61670000
O	-0.01370000	-1.49490000	-0.70040000
O	0.09340000	1.89330000	-0.88640000
O	1.97970000	0.44330000	0.46650000
O	0.32300000	1.51770000	2.57820000
O	-2.24110000	-0.04120000	-0.56700000
O	0.85090000	-1.35580000	1.96350000
O	-1.82800000	2.14160000	1.07170000
O	-1.88530000	-0.62730000	2.15560000
N	-0.50550000	-1.65830000	-1.96910000
C	-2.75120000	-1.08600000	-1.02300000
N	1.13250000	2.34660000	-1.64620000
C	2.81680000	1.15440000	-0.13050000
C	-0.30350000	-0.42250000	-2.80200000
C	-1.96610000	-2.04680000	-1.89400000
C	0.12340000	-2.90450000	-2.61720000
N	-4.00930000	-1.39660000	-0.73560000
C	-4.71280000	-0.63070000	0.25910000
C	2.41920000	2.42650000	-0.84260000
C	1.24670000	1.56760000	-2.93210000
C	0.92770000	3.83760000	-1.99030000
N	4.10940000	0.88060000	-0.07280000
C	4.63260000	-0.22720000	0.68230000
C	1.14410000	0.05750000	-2.77750000
C	1.59670000	-3.13290000	-2.28060000
C	-0.67450000	-4.08820000	-2.03140000
C	1.65300000	-4.59770000	-1.81780000
C	0.31610000	-4.80410000	-1.10940000
C	-1.93090000	-3.48990000	-1.38610000
C	-4.88200000	-1.22560000	1.52810000
C	-5.10870000	0.68010000	-0.03630000
C	-5.61960000	1.44190000	1.02300000
C	-5.07570000	1.25750000	-1.43810000
C	-5.75200000	0.90640000	2.29780000
C	-5.40840000	-0.42160000	2.54340000
C	-4.57370000	-2.69830000	1.74470000
C	-6.50310000	1.55360000	-1.91300000
C	-4.19500000	2.50510000	-1.54190000
C	-4.35610000	-3.07930000	3.20660000
C	-5.69510000	-3.55730000	1.14230000
C	-0.51680000	4.21530000	-2.30460000
C	1.35890000	4.59140000	-0.71970000
C	-0.81680000	5.39240000	-1.35850000
C	0.05690000	5.14070000	-0.12800000
C	2.15420000	3.58360000	0.12320000
C	4.60760000	-0.17060000	2.08480000
C	5.15640000	-1.31250000	-0.04000000
C	5.11440000	-1.27700000	2.77140000
C	4.15780000	1.05880000	2.85040000
C	5.63170000	-2.37010000	2.08780000

C	5.65820000	-2.38470000	0.69750000
C	5.21890000	-1.28120000	-1.55530000
C	5.27840000	-2.66700000	-2.19250000
C	6.41600000	-0.44070000	-2.02190000
C	5.37750000	1.85490000	3.32840000
C	3.24010000	0.72000000	4.02750000
H	-4.41100000	-2.25810000	-1.08460000
H	4.75700000	1.44720000	-0.60730000
H	-0.63730000	-0.65710000	-3.81640000
H	-0.96230000	0.33520000	-2.38020000
H	1.71140000	-0.39840000	-3.59340000
H	1.61420000	-0.27270000	-1.84940000
H	0.44880000	1.95250000	-3.57310000
H	2.19920000	1.85520000	-3.38380000
H	-0.05980000	-2.77960000	-3.68780000
H	1.87650000	-2.47930000	-1.45050000
H	2.25460000	-2.92380000	-3.12700000
H	1.72970000	-5.26870000	-2.68000000
H	2.51510000	-4.79890000	-1.17700000
H	0.32940000	-4.30740000	-0.13060000
H	0.06580000	-5.85540000	-0.95110000
H	-0.95150000	-4.75640000	-2.85240000
H	-1.84900000	-3.49740000	-0.29570000
H	-2.84260000	-4.02510000	-1.66220000
H	-2.35320000	-2.01180000	-2.92060000
H	-5.95140000	2.45900000	0.83500000
H	-6.16160000	1.51310000	3.09950000
H	-5.56860000	-0.83930000	3.53140000
H	-4.65860000	0.49950000	-2.11040000
H	-6.49320000	1.88950000	-2.95360000
H	-6.96860000	2.34250000	-1.31480000
H	-7.13800000	0.66650000	-1.84720000
H	-3.15080000	2.26770000	-1.31150000
H	-4.54080000	3.29870000	-0.87080000
H	-4.22980000	2.90770000	-2.55840000
H	-3.64270000	-2.92640000	1.20490000
H	-4.03270000	-4.12080000	3.27480000
H	-5.27700000	-2.99450000	3.79040000
H	-3.59340000	-2.46090000	3.69280000
H	-6.63770000	-3.37140000	1.66500000
H	-5.46010000	-4.62080000	1.23810000
H	-5.87650000	-3.34530000	0.08240000
H	1.60940000	4.01630000	-2.82680000
H	-1.16820000	3.36470000	-2.08360000
H	-0.65410000	4.47750000	-3.35580000
H	-1.88120000	5.48070000	-1.12560000
H	-0.52100000	6.33400000	-1.83170000
H	0.21330000	6.03980000	0.47230000
H	-0.39280000	4.38980000	0.53470000
H	2.00070000	5.42650000	-1.01560000
H	3.09690000	3.98280000	0.50340000
H	1.56880000	3.22550000	0.97460000

H	3.19270000	2.71260000	-1.56330000
H	5.13240000	-1.27150000	3.85680000
H	6.03400000	-3.21160000	2.64300000
H	6.08040000	-3.24020000	0.18230000
H	4.29770000	-0.79380000	-1.91160000
H	6.44260000	-0.37290000	-3.11320000
H	7.35180000	-0.89980000	-1.69080000
H	6.41070000	0.58090000	-1.62330000
H	5.17370000	-2.58490000	-3.27800000
H	4.48820000	-3.32390000	-1.81770000
H	6.23940000	-3.15530000	-2.00670000
H	3.59220000	1.70700000	2.17170000
H	6.01900000	2.14350000	2.49120000
H	5.98390000	1.25970000	4.01740000
H	5.06820000	2.76420000	3.85230000
H	2.41960000	0.05070000	3.73430000
H	2.83860000	1.63880000	4.47240000
H	3.77520000	0.20930000	4.83280000
H	-1.66570000	2.80520000	0.38660000
H	-2.85570000	-0.62200000	2.05910000
H	0.65150000	-2.29100000	1.83830000
H	1.02800000	1.33840000	3.21550000
H	-0.31180000	2.12610000	2.97430000
H	-1.68760000	-0.85190000	3.07160000
H	1.79680000	-1.25000000	1.77210000
H	-2.77520000	1.94170000	1.02430000

L_3-PrPr$_2$/Tb^{3+}

Tb	0.02380000	0.03800000	-0.97080000
O	0.10080000	1.76300000	0.48610000
O	-0.15620000	-1.76070000	0.50240000
O	-2.19760000	0.60950000	-0.48260000
O	2.16560000	-0.45050000	-0.19600000
O	1.84720000	1.36270000	-2.01670000
O	-1.56470000	-1.76060000	-1.68680000
O	0.91600000	-1.36980000	-2.81030000
O	-0.91920000	1.14390000	-2.97430000
N	-0.70230000	2.48290000	1.32110000
C	-2.77020000	1.39470000	0.30460000
N	0.62610000	-2.41460000	1.41840000
C	2.74740000	-1.30070000	0.50990000
C	-2.10180000	2.67450000	0.75260000
C	-0.20130000	3.90670000	1.33720000
C	-0.68110000	1.91130000	2.71510000
N	-4.01540000	1.18400000	0.69710000
C	-4.79480000	0.06910000	0.21960000
C	0.18190000	-3.85740000	1.45580000
C	2.06270000	-2.57490000	0.94450000
C	0.49430000	-1.80600000	2.79070000
N	4.02680000	-1.16310000	0.81270000
C	4.81010000	-0.07870000	0.27260000

C	-0.78390000	0.39460000	2.76320000
C	0.58390000	-0.28840000	2.82030000
C	-0.64330000	4.48500000	0.00290000
C	-1.88730000	3.66300000	-0.39970000
C	-5.30370000	0.11330000	-1.08960000
C	-5.01260000	-1.00800000	1.09080000
C	-6.05170000	-0.98410000	-1.51930000
C	-5.09160000	1.28970000	-2.02140000
C	-6.28830000	-2.06620000	-0.67930000
C	-5.77500000	-2.07510000	0.61100000
C	-4.45690000	-1.05080000	2.50020000
C	-4.35900000	0.85680000	-3.29480000
C	-6.41510000	1.98040000	-2.36170000
C	-5.57440000	-1.14630000	3.54230000
C	-3.45620000	-2.20080000	2.65310000
C	0.73160000	-4.46710000	0.17410000
C	1.94690000	-3.59120000	-0.19850000
C	5.31200000	-0.20560000	-1.03420000
C	5.02000000	1.05430000	1.07160000
C	5.78060000	2.08920000	0.52320000
C	4.43460000	1.19430000	2.46220000
C	6.29890000	1.99420000	-0.76210000
C	6.06270000	0.86120000	-1.53240000
C	5.09840000	-1.44170000	-1.88620000
C	5.50880000	1.48590000	3.51170000
C	3.34240000	2.27060000	2.47070000
C	6.41300000	-2.20150000	-2.08910000
C	4.45570000	-1.09500000	-3.23290000
H	-4.45150000	1.84700000	1.32640000
H	4.48300000	-1.86170000	1.38710000
H	0.26350000	2.24740000	3.15010000
H	-1.49230000	2.39900000	3.26170000
H	-1.36170000	0.00620000	1.92050000
H	-1.35060000	0.12830000	3.66220000
H	1.07690000	-0.00720000	3.75740000
H	1.22320000	0.09070000	2.02010000
H	-0.47620000	-2.14380000	3.16260000
H	1.26830000	-2.27390000	3.40460000
H	0.87570000	3.85620000	1.49340000
H	-0.67520000	4.40750000	2.18700000
H	0.14370000	4.37930000	-0.74450000
H	-0.86610000	5.54850000	0.10150000
H	-2.77900000	4.27930000	-0.53120000
H	-1.71300000	3.12070000	-1.33070000
H	-2.67480000	3.14490000	1.55750000
H	-6.47680000	-0.98230000	-2.51860000
H	-6.88740000	-2.90090000	-1.02950000
H	-5.97960000	-2.91990000	1.26180000
H	-4.46180000	2.02830000	-1.51200000
H	-6.24260000	2.84910000	-3.00370000
H	-6.92940000	2.31920000	-1.45880000
H	-7.09030000	1.30380000	-2.89310000

H	-4.07490000	1.72730000	-3.89720000
H	-4.98650000	0.22540000	-3.93030000
H	-3.46940000	0.25750000	-3.05240000
H	-3.90960000	-0.11720000	2.68310000
H	-5.16020000	-1.11950000	4.55430000
H	-6.13490000	-2.08000000	3.44030000
H	-6.28630000	-0.32260000	3.44320000
H	-2.63970000	-2.11160000	1.92590000
H	-3.94230000	-3.16910000	2.49980000
H	-3.03440000	-2.20600000	3.66440000
H	0.62050000	-4.30830000	2.35090000
H	-0.90370000	-3.85050000	1.55040000
H	-0.01230000	-4.45400000	-0.62430000
H	1.01040000	-5.50910000	0.33950000
H	2.87270000	-4.16360000	-0.28440000
H	1.78170000	-3.06910000	-1.14290000
H	2.59310000	-3.01670000	1.79400000
H	5.97850000	2.97780000	1.11490000
H	6.89990000	2.80410000	-1.16380000
H	6.48810000	0.79530000	-2.52930000
H	3.96010000	0.24210000	2.73150000
H	2.55860000	2.04890000	1.73640000
H	3.76480000	3.25180000	2.23100000
H	2.89090000	2.34440000	3.46670000
H	5.06720000	1.51330000	4.51190000
H	5.98720000	2.45430000	3.33950000
H	6.29180000	0.72340000	3.50560000
H	6.24800000	-3.11080000	-2.67420000
H	4.41090000	-2.11310000	-1.35780000
H	6.86200000	-2.48570000	-1.13370000
H	7.14190000	-1.58740000	-2.62580000
H	3.56840000	-0.46110000	-3.10150000
H	4.18490000	-2.00820000	-3.77400000
H	5.14210000	-0.53960000	-3.87820000
H	1.89080000	2.27040000	-2.33530000
H	-1.43630000	-2.30950000	-0.89370000
H	2.66370000	1.18870000	-1.52230000
H	-1.87520000	1.18510000	-3.12200000
H	-0.50330000	1.15890000	-3.84430000
H	0.34220000	-1.98250000	-3.28560000
H	1.76610000	-1.32360000	-3.26620000
H	-2.49950000	-1.51090000	-1.68480000

L_3-PiPr$_2$/Tb^{3+}

Tb	0.00040000	0.00320000	-0.93320000
O	-0.06420000	-1.51910000	0.75950000
O	2.23920000	-0.58240000	-0.45550000
O	0.06640000	1.52150000	0.76640000
O	-2.23690000	0.54160000	-0.41570000
N	0.83300000	-1.83700000	1.74400000
N	4.13860000	-1.08910000	0.61840000

H	4.60400000	-1.66800000	1.30700000
N	-0.82940000	1.82500000	1.75760000
N	-4.14530000	1.07540000	0.62720000
H	-4.61440000	1.66130000	1.30730000
C	1.16380000	-0.63230000	2.59260000
H	1.59430000	0.10450000	1.91510000
H	1.92890000	-0.96010000	3.30290000
C	0.01640000	-0.00570000	3.36930000
H	-0.43400000	-0.73590000	4.04920000
H	0.47750000	0.72810000	4.03810000
C	-1.14300000	0.61540000	2.60610000
H	-1.90260000	0.93720000	3.32510000
H	-1.57590000	-0.12230000	1.93130000
C	0.22200000	-2.94050000	2.58020000
H	-0.70550000	-2.52880000	2.97620000
H	0.91530000	-3.13900000	3.40480000
C	-0.04960000	-4.17820000	1.75020000
H	-0.47240000	-4.93450000	2.41840000
H	-0.81660000	-3.93900000	1.00780000
C	1.21270000	-4.69610000	1.07470000
H	0.97690000	-5.53710000	0.41750000
H	1.91410000	-5.07740000	1.82740000
C	1.87840000	-3.58400000	0.27250000
H	2.83920000	-3.91500000	-0.13590000
H	1.25260000	-3.27330000	-0.56980000
C	2.14040000	-2.36980000	1.15730000
H	2.74170000	-2.66860000	2.02360000
C	2.84870000	-1.26980000	0.39380000
C	4.90010000	-0.06680000	-0.05490000
C	5.30910000	-0.28070000	-1.38100000
C	6.04900000	0.73450000	-1.99060000
H	6.40080000	0.60070000	-3.00900000
C	6.36240000	1.90380000	-1.30810000
H	6.95030000	2.67370000	-1.79780000
C	5.93820000	2.08590000	0.00250000
H	6.19830000	3.00070000	0.52580000
C	5.19790000	1.10330000	0.66240000
C	4.99810000	-1.55110000	-2.14490000
H	4.32550000	-2.16610000	-1.53540000
C	4.27740000	-1.24130000	-3.46070000
H	3.46470000	-0.51590000	-3.31020000
H	3.89120000	-2.15920000	-3.91820000
H	4.94890000	-0.78720000	-4.19510000
C	6.26630000	-2.37200000	-2.39610000
H	6.76460000	-2.63240000	-1.45870000
H	6.98140000	-1.81290000	-3.00650000
H	6.02830000	-3.29890000	-2.92610000
C	4.72930000	1.33190000	2.08660000
H	4.31200000	0.39060000	2.46690000
C	5.87760000	1.72800000	3.01660000
H	5.52330000	1.80180000	4.04870000
H	6.29820000	2.70090000	2.74720000

H	6.68810000	0.99550000	2.98590000
C	3.60640000	2.37550000	2.11930000
H	3.25640000	2.52440000	3.14730000
H	2.75370000	2.08060000	1.49470000
H	3.96630000	3.34340000	1.75620000
C	-0.22600000	2.93270000	2.59390000
H	0.70810000	2.53010000	2.98350000
H	-0.91680000	3.12090000	3.42310000
C	0.02690000	4.17670000	1.76750000
H	0.79360000	3.94980000	1.02090000
H	0.44400000	4.93540000	2.43640000
C	-1.24440000	4.68230000	1.09970000
H	-1.94570000	5.05360000	1.85740000
H	-1.02160000	5.52790000	0.44390000
C	-1.90270000	3.56530000	0.29820000
H	-1.28030000	3.26360000	-0.54980000
H	-2.86980000	3.88720000	-0.10240000
C	-2.14580000	2.34540000	1.18110000
H	-2.74430000	2.63580000	2.05220000
C	-4.90850000	0.06120000	-0.05650000
C	-5.30550000	0.28460000	-1.38460000
C	-6.04810000	-0.72230000	-2.00480000
H	-6.39140000	-0.58090000	-3.02520000
C	-6.37530000	-1.89230000	-1.33020000
H	-6.96540000	-2.65550000	-1.82780000
C	-5.96170000	-2.08430000	-0.01750000
H	-6.23130000	-3.00030000	0.49870000
C	-5.21890000	-1.11060000	0.65250000
C	-4.97770000	1.55570000	-2.14060000
H	-4.31490000	2.16780000	-1.51750000
C	-4.23260000	1.24550000	-3.44270000
H	-3.41790000	0.52660000	-3.27450000
H	-3.84540000	2.16510000	-3.89670000
H	-4.88880000	0.78520000	-4.18700000
C	-6.23850000	2.38040000	-2.41470000
H	-6.75470000	2.63920000	-1.48660000
H	-6.94290000	1.82540000	-3.04100000
H	-5.98770000	3.30840000	-2.93680000
C	-4.75260000	-1.35120000	2.07530000
H	-4.35510000	-0.40760000	2.47090000
C	-3.60900000	-2.37290000	2.09360000
H	-2.76410000	-2.05470000	1.47000000
H	-3.95170000	-3.34270000	1.71890000
H	-3.25420000	-2.52740000	3.11910000
C	-5.89380000	-1.78450000	2.99690000
H	-6.72060000	-1.07020000	2.97290000
H	-5.54010000	-1.86190000	4.02890000
H	-6.29110000	-2.76390000	2.71620000
O	1.73080000	1.58450000	-1.76780000
H	1.74180000	2.54690000	-1.73280000
O	-1.72620000	-1.53030000	-1.84660000
H	-1.73790000	-2.48440000	-1.97520000

O	0.90520000	-1.31390000	-2.83480000
H	0.44130000	-1.53040000	-3.65140000
H	1.85280000	-1.36030000	-3.02760000
O	-0.88330000	1.40590000	-2.78020000
H	-1.81820000	1.42510000	-3.03100000
H	-0.37730000	1.71100000	-3.54170000
H	2.59450000	1.27480000	-1.45270000
H	-2.59150000	-1.26920000	-1.49490000
C	-2.85090000	1.24220000	0.41880000

L_3-PiPr$_3$/Tb^{3+}

Tb	-0.10410000	-0.12940000	-0.54240000
O	0.28740000	1.64740000	0.86090000
O	-2.06680000	1.10340000	-0.37710000
O	-0.38630000	-1.30080000	1.43060000
O	2.01900000	-0.78440000	0.16590000
N	-0.52740000	2.31820000	1.73290000
N	-3.88000000	1.99840000	0.55960000
H	-4.29790000	2.72040000	1.13350000
N	0.47980000	-1.52350000	2.47240000
N	3.86880000	-1.50670000	1.18910000
H	4.28340000	-2.05180000	1.93540000
C	-1.11560000	1.36970000	2.74840000
H	-1.67640000	0.62910000	2.17890000
H	-1.81330000	1.95600000	3.35430000
C	-0.13440000	0.67480000	3.68080000
H	0.39790000	1.41380000	4.28810000
H	-0.74920000	0.13260000	4.40610000
C	0.94230000	-0.22720000	3.09590000
H	1.63430000	-0.51040000	3.89460000
H	1.48710000	0.30660000	2.31820000
C	0.30170000	3.38820000	2.40940000
H	1.11690000	2.85910000	2.90140000
H	-0.33790000	3.85870000	3.16450000
C	0.83890000	4.39150000	1.41010000
H	1.41870000	5.13190000	1.96930000
H	1.53210000	3.87780000	0.73760000
C	-0.28070000	5.05770000	0.62330000
H	0.13160000	5.71940000	-0.14280000
H	-0.88790000	5.68750000	1.28560000
C	-1.16030000	3.99910000	-0.02980000
H	-2.02330000	4.45310000	-0.52880000
H	-0.60040000	3.43710000	-0.78390000
C	-1.68710000	3.01620000	1.01080000
H	-2.23340000	3.55520000	1.79300000
C	-2.57080000	1.97150000	0.36790000
C	-4.68480000	0.95720000	-0.03090000
C	-4.95620000	1.01330000	-1.41020000
C	-5.58460000	-0.08880000	-1.98070000
H	-5.81470000	-0.07470000	-3.04100000
C	-5.93910000	-1.21810000	-1.23120000

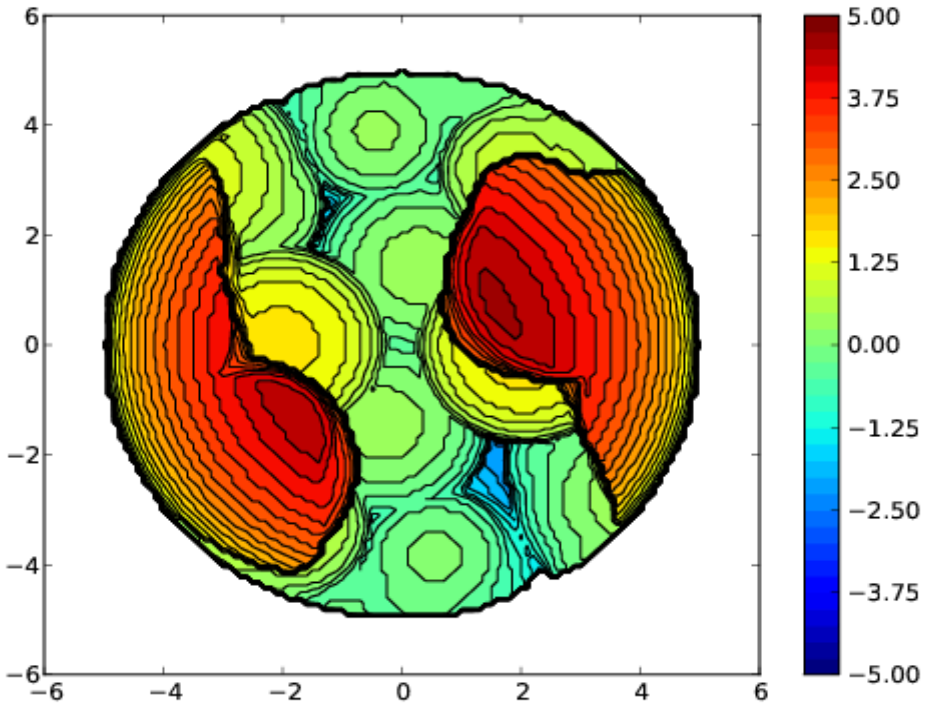
C	-5.66750000	-1.21460000	0.13540000
H	-5.97240000	-2.07230000	0.73000000
C	-5.03880000	-0.13600000	0.76740000
C	-4.61490000	2.24410000	-2.22840000
H	-3.66710000	2.65160000	-1.84860000
C	-4.41770000	1.95610000	-3.71550000
H	-3.73410000	1.11530000	-3.89570000
H	-4.02030000	2.83920000	-4.22230000
H	-5.36050000	1.70520000	-4.21000000
C	-5.68940000	3.32050000	-2.03040000
H	-5.80600000	3.59140000	-0.97660000
H	-6.65940000	2.96090000	-2.38570000
H	-5.43920000	4.22690000	-2.58900000
C	-4.79950000	-0.17590000	2.26450000
H	-4.27910000	0.74580000	2.55440000
C	-6.12950000	-0.21140000	3.02380000
H	-5.95770000	-0.17130000	4.10330000
H	-6.68310000	-1.13010000	2.80900000
H	-6.76840000	0.63130000	2.74780000
C	-3.90550000	-1.35090000	2.67020000
H	-3.75580000	-1.35570000	3.75530000
H	-2.92080000	-1.29880000	2.18870000
H	-4.36420000	-2.30930000	2.40710000
C	-0.24250000	-2.37840000	3.49200000
H	-1.11950000	-1.80460000	3.78840000
H	0.42870000	-2.48480000	4.35090000
C	-0.64260000	-3.72310000	2.92050000
H	-1.39380000	-3.57140000	2.13950000
H	-1.13160000	-4.28580000	3.72140000
C	0.55440000	-4.48680000	2.37270000
H	1.21650000	-4.78540000	3.19510000
H	0.22870000	-5.41000000	1.88640000
C	1.32700000	-3.62310000	1.38320000
H	0.73700000	-3.41600000	0.48510000
H	2.24620000	-4.12430000	1.06210000
C	1.72030000	-2.29410000	2.02240000
H	2.28690000	-2.48290000	2.94170000
C	2.55310000	-1.45690000	1.07270000
C	4.72280000	-0.78570000	0.27940000
C	4.94760000	-1.30680000	-1.00590000
C	5.74640000	-0.55840000	-1.86740000
H	5.95370000	-0.94760000	-2.86060000
C	6.31540000	0.66080000	-1.48760000
C	6.06050000	1.13430000	-0.20130000
H	6.50280000	2.07900000	0.10270000
C	5.26540000	0.43340000	0.70650000
C	4.39180000	-2.64210000	-1.45950000
H	3.68760000	-2.99970000	-0.69860000
C	3.61900000	-2.51500000	-2.77540000
H	2.90230000	-1.68340000	-2.73870000
H	3.10310000	-3.45390000	-3.01090000
H	4.28310000	-2.31120000	-3.62020000

C	5.50620000	-3.68590000	-1.57920000
H	6.03700000	-3.81200000	-0.63180000
H	6.24190000	-3.38640000	-2.33140000
H	5.09990000	-4.65740000	-1.87600000
C	4.97050000	1.01530000	2.07500000
H	4.51960000	0.22720000	2.69210000
C	3.94220000	2.14660000	1.95210000
H	3.02510000	1.81270000	1.45140000
H	4.35360000	2.97600000	1.36760000
H	3.68650000	2.53940000	2.94300000
C	6.23110000	1.49080000	2.79770000
H	6.97650000	0.69460000	2.86690000
H	5.98620000	1.81720000	3.81240000
H	6.69480000	2.33980000	2.28770000
O	-2.06050000	-1.68780000	-0.61640000
H	-2.06280000	-2.12760000	0.24550000
O	1.76450000	0.73700000	-1.88480000
H	1.89440000	1.40550000	-2.56500000
O	-1.04850000	0.47670000	-2.75600000
H	-0.85480000	0.15960000	-3.64470000
H	-1.92210000	0.88870000	-2.77760000
O	0.35750000	-2.15640000	-1.87990000
H	1.17830000	-2.44150000	-2.30330000
H	-0.35720000	-2.73740000	-2.16450000
C	-6.59110000	-2.41100000	-1.89140000
C	-5.62920000	-3.06940000	-2.88490000
C	-7.91350000	-2.03400000	-2.56280000
H	-6.81030000	-3.13930000	-1.10070000
H	-4.68840000	-3.35750000	-2.40190000
H	-6.07860000	-3.97050000	-3.31070000
H	-5.39560000	-2.39480000	-3.71600000
H	-8.60440000	-1.57030000	-1.85390000
H	-7.75890000	-1.33620000	-3.39240000
H	-8.39560000	-2.92610000	-2.97110000
C	7.18450000	1.44190000	-2.44650000
C	6.38770000	1.88410000	-3.67660000
C	8.42780000	0.64390000	-2.84710000
H	7.51850000	2.34400000	-1.91930000
H	5.51270000	2.48000000	-3.39550000
H	7.01200000	2.49520000	-4.33390000
H	6.04500000	1.02210000	-4.25970000
H	9.00590000	0.33710000	-1.97140000
H	8.16140000	-0.25690000	-3.41030000
H	9.07560000	1.25050000	-3.48550000
H	2.62600000	0.52380000	-1.49370000
H	-2.95400000	-1.32840000	-0.73360000

%V Free	%V Buried	% V Tot/V Ex
30.9	**69.1**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	27.6	103.2	130.8	**21.1**	78.9
NW	51.3	79.5	130.8	**39.2**	60.8
NE	28.5	102.3	130.8	**21.8**	78.2
SE	54.2	76.7	130.8	**41.4**	58.6

Steric Map



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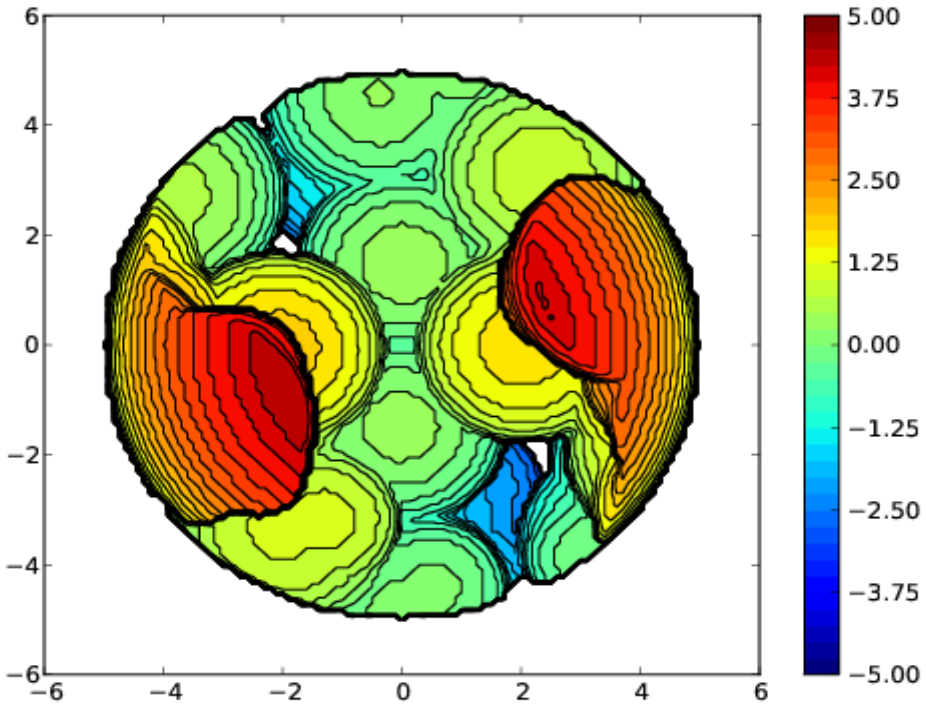
Sc-L$_3$-RaPr$_2$

%V Free	%V Buried	% V Tot/V Ex
36.2	**63.8**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	33.1	97.7	130.8	**25.3**	74.7
NW	58.3	72.5	130.8	**44.6**	55.4
NE	37.9	92.9	130.8	**29.0**	71.0
SE	59.9	70.9	130.8	**45.8**	54.2

Steric Map



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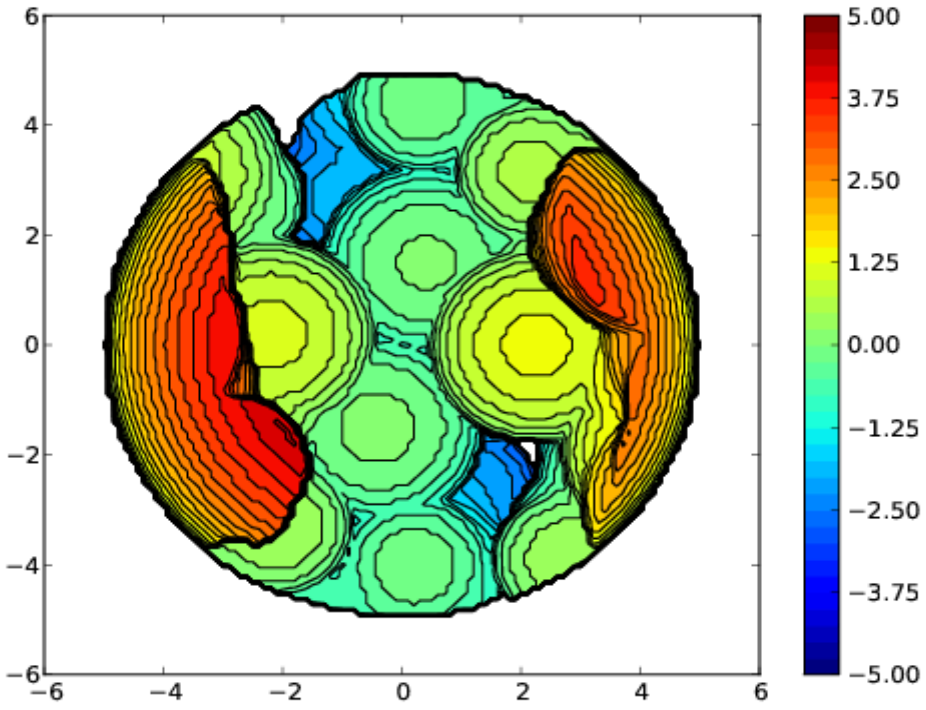
Ni-**L₃-RaPr₂**

%V Free	%V Buried	% V Tot/V Ex
40.4	**59.6**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	43.1	87.7	130.8	**33.0**	67.0
NW	61.5	69.3	130.8	**47.1**	52.9
NE	45.8	85.0	130.8	**35.0**	65.0
SE	60.7	70.1	130.8	**46.4**	53.6

Steric Map



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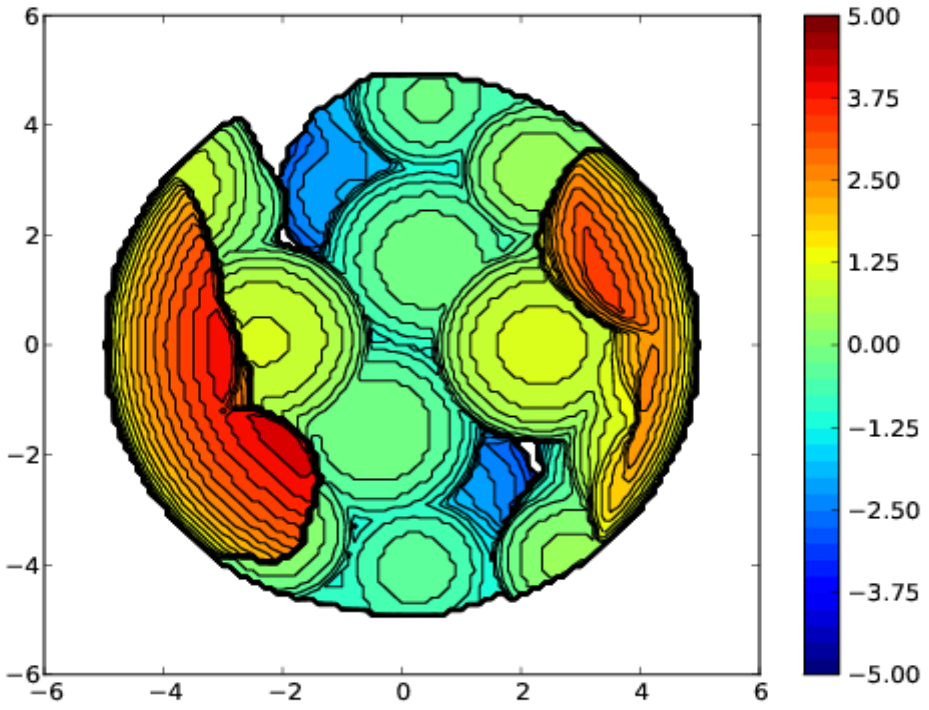
Y-**L_3-RaPr$_2$**

%V Free	%V Buried	% V Tot/V Ex
43.4	**56.6**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	43.4	87.4	130.8	**33.2**	66.8
NW	69.1	61.7	130.8	**52.9**	47.1
NE	50.0	80.8	130.8	**38.2**	61.8
SE	64.8	66.0	130.8	**49.6**	50.4

Steric Map



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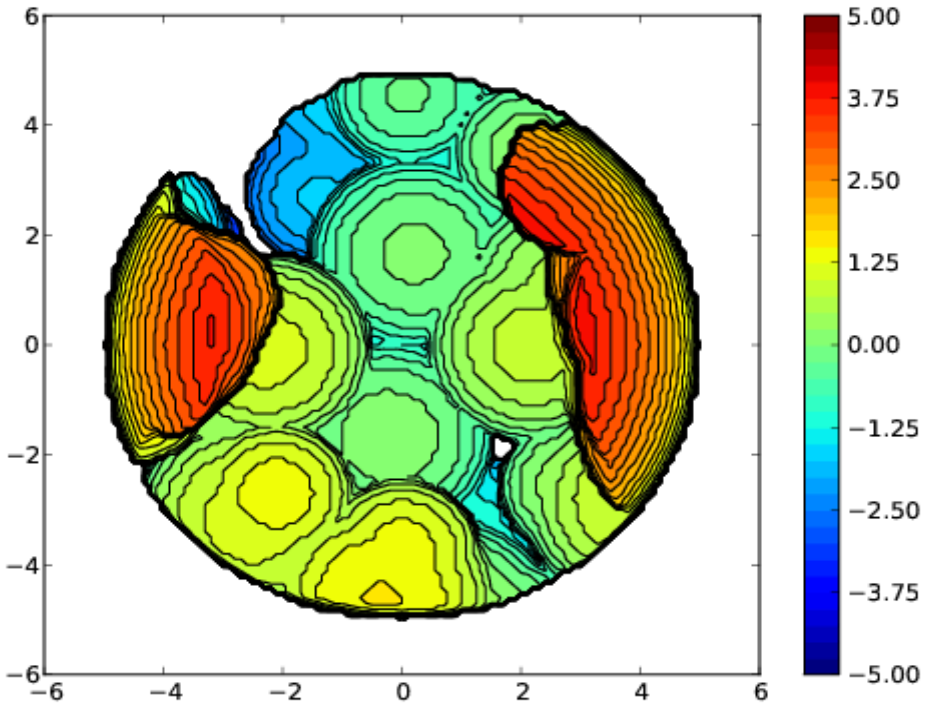
Nd-**L₃-RaPr₂**

%V Free	%V Buried	% V Tot/V Ex
40.6	**59.4**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	43.4	87.4	130.8	**33.2**	66.8
NW	66.7	64.2	130.8	**51.0**	49.0
NE	45.1	85.7	130.8	**34.5**	65.5
SE	57.2	73.6	130.8	**43.7**	56.3

Steric Map



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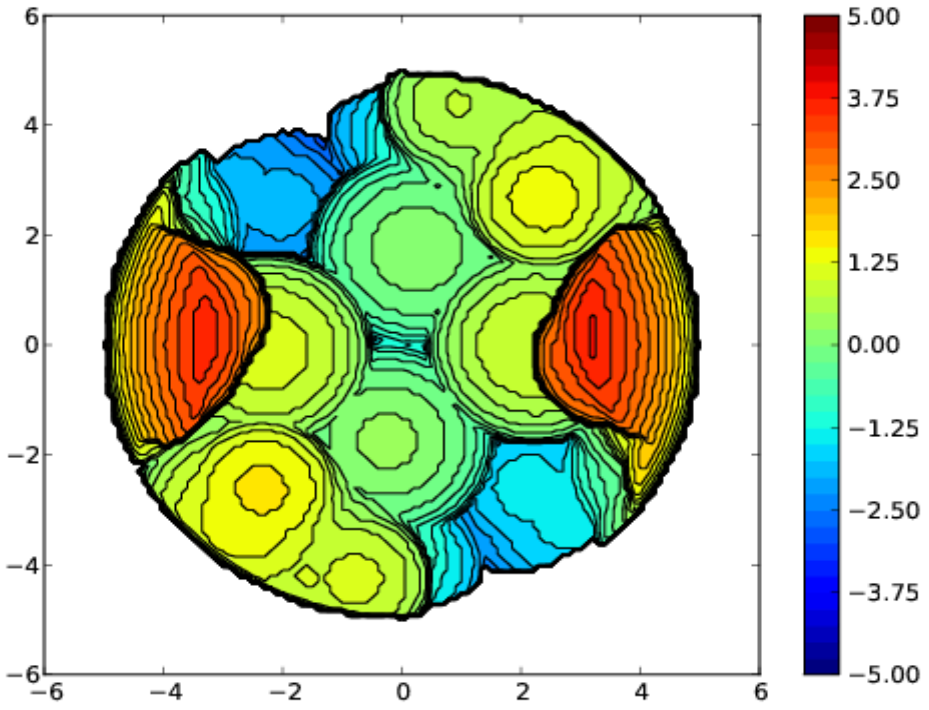
Tb-**L$_3$-RaPr$_2$**

%V Free	%V Buried	% V Tot/V Ex
42.2	**57.8**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	43.5	87.3	130.8	**33.2**	66.8
NW	67.3	63.5	130.8	**51.5**	48.5
NE	45.4	85.4	130.8	**34.7**	65.3
SE	64.5	66.3	130.8	**49.3**	50.7

Steric Map



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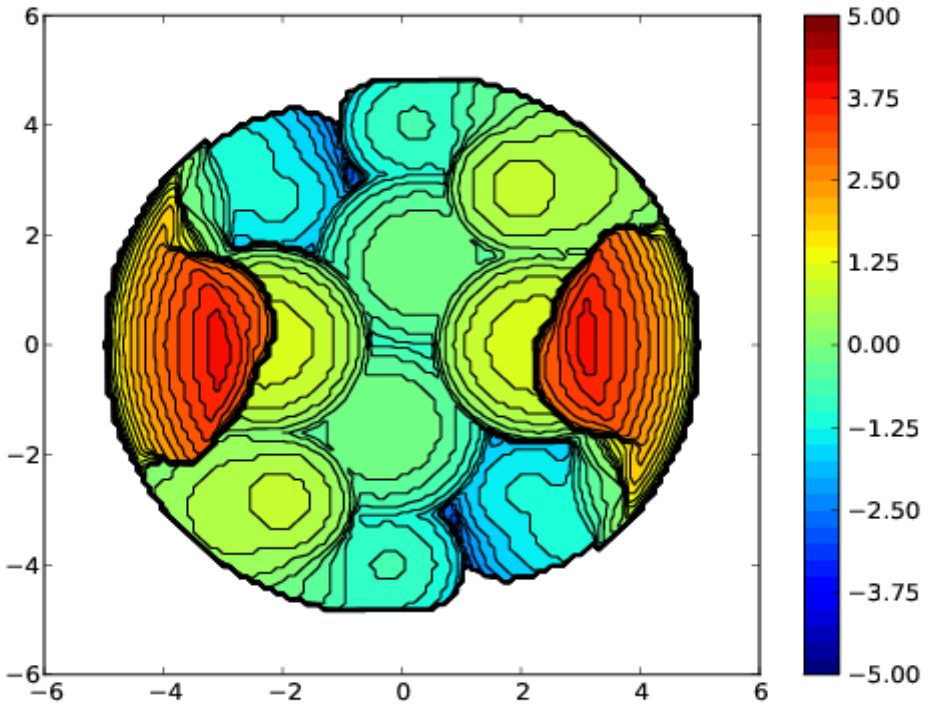
Tb-**L$_3$-PrPr$_2$**

%V Free	%V Buried	% V Tot/V Ex
44.1	**55.9**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	51.3	79.5	130.8	**39.3**	60.7
NW	63.9	66.9	130.8	**48.9**	51.1
NE	51.2	79.6	130.8	**39.2**	60.8
SE	64.4	66.4	130.8	**49.2**	50.8

Steric Map



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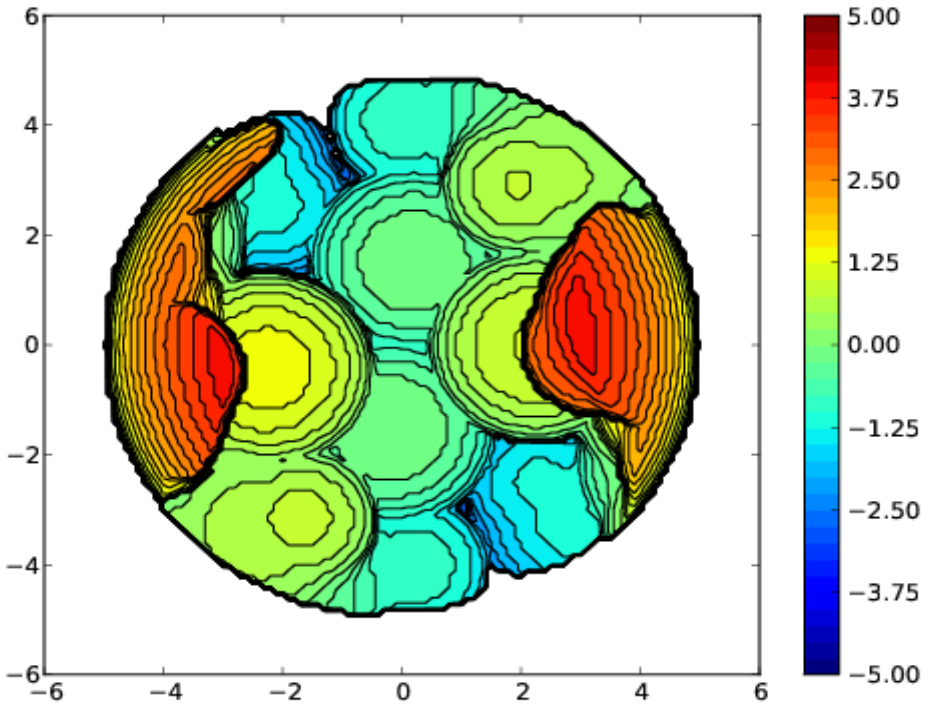
Tb-**L$_3$-PiPr$_2$**

%V Free	%V Buried	% V Tot/V Ex
43.1	**56.9**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	47.4	83.4	130.8	**36.2**	63.8
NW	64.2	66.6	130.8	**49.1**	50.9
NE	49.2	81.6	130.8	**37.6**	62.4
SE	64.7	66.1	130.8	**49.5**	50.5

Steric Map



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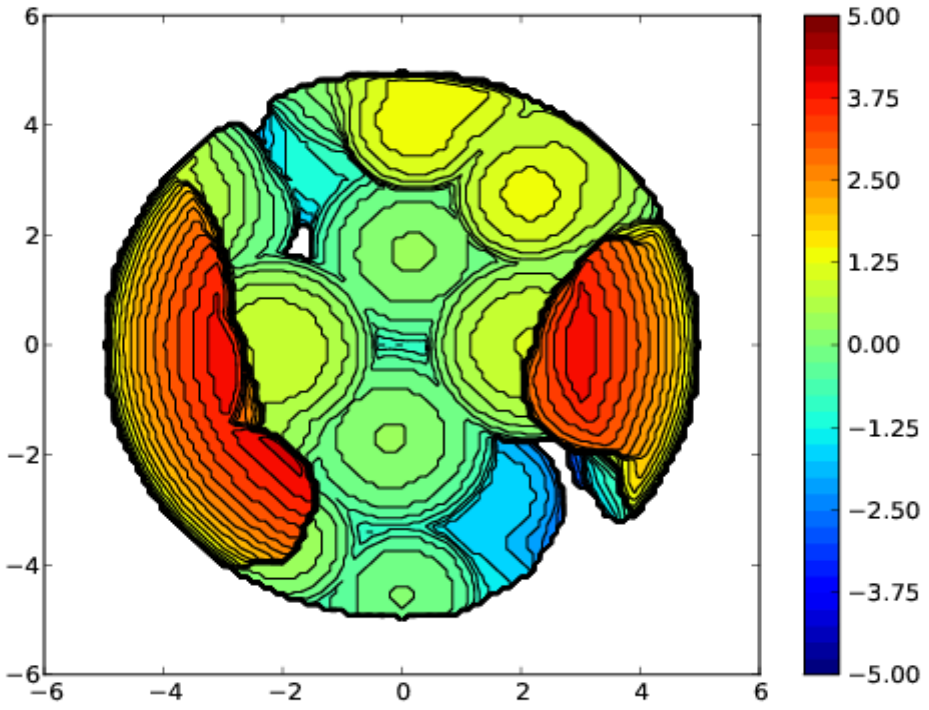
Tb-**L$_3$-PiPr$_3$**

%V Free	%V Buried	% V Tot/V Ex
39.9	**60.1**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	41.4	89.4	130.8	**31.7**	68.3
NW	60.4	70.4	130.8	**46.2**	53.8
NE	42.6	88.2	130.8	**32.6**	67.4
SE	64.1	66.7	130.8	**49.0**	51.0

Steric Map



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Yb-**L$_3$-RaPr$_2$**